Carbohydrate Research, 210 (1991) 155–166
Elsevier Science Publishers B.V., Amsterdam

Transformation of aldoses into glycosylamine 1,2-(cyclic carbamates) (glyco-oxazolidin-2-ones) by reaction with potassium cyanate

József Kovács*, István Pintér,
Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest (Hungary)

Ursula Lendering, and Peter Köll
University of Oldenburg, Department of Chemistry, Organic Chemistry Laboratory, C.-v.-Ossietzky-Str. 9-11, D-2900 Oldenburg (F.R.G.)

(Received May 31st, 1990; accepted for publication, July 20th, 1990)

ABSTRACT

Treatment of pentoses and some hexoses with potassium cyanate in aqueous solutions, buffered with sodium dihydrogen phosphate or ammonium chloride, gave glycosylamine 1,2-(cyclic carbamates) {glyco-furano(or pyrano)[1,2-*d*]oxazolidin-2-ones}. Most of the products had furanoid structures, but D-mannose and D-lyxose gave preponderantly pyranose derivatives. Epimerisation at C-2 was observed in certain reactions. The products and their acetylated derivatives were characterised by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

INTRODUCTION

Cyclic carbamates (glyco-oxazolidin-2-one derivatives) of amino sugars have attracted interest since they enable simultaneous protection of amino and hydroxyl groups[1]. These compounds, as well as the analogous cyclic urea derivatives which are potential components of some aminoglycoside antibiotics[2,3], are accessible easily by a one-pot procedure[4,5] starting from azido sugars. However, the easy accessibility of cyclic 1,2-thiocarbamates of glycosylamines by the reaction[6] of sugars with potassium thiocyanate under strongly acidic conditions prompted a study of the reaction of aldoses with potassium cyanate, expected to afford the corresponding oxazolidin-2-ones.

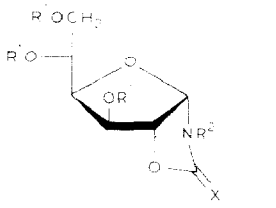
RESULTS AND DISCUSSION

2-Amino-2-deoxy-D-glucose hydrochloride reacted[7] with potassium cyanate to give the imidazolidin-2-one derivative. Similar treatment of aldoses with aqueous potassium cyanate gave complex mixtures due to the alkalinity of the solution (pH 9→12.5). However, when an aqueous solution of D-glucose and potassium cyanate (1.5 mol) was buffered with either sodium dihydrogen phosphate (0.55 mol, pH 7) or ammonium chloride (1.5 mol, pH 7) then, after reaction for 6 h at 60°, 30–34% of

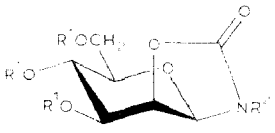
* Author for correspondence.

0008-6215/91/$ 03.50

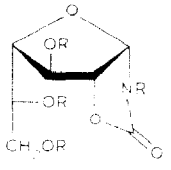
α-D-glucofuranosylamine 1,2-(cyclic carbamate) (**1**) was obtained. The ^{13}C-n.m.r. spectrum of the reaction mixture revealed much unreacted glucose even after prolonged reaction. Compound **1** was identical with the product obtained by desulfuration of the thiocarbamate[8] **2** with hydrogen peroxide, and its structure was corroborated by the ^{1}H- and ^{13}C-n.m.r. data (Tables I and II). The $J_{2,3}$ value of 0 Hz is characteristic for the furanoid structure with the *trans*-arrangement of H-2,3, as found[6] for **2**.



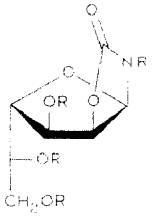
1 R^1 = R^2 = H, X = O
2 R^1 = R^2 = H, X = S
3 R^1 = Ac, R^2 = H, X = O
4 R^1 = R^2 = Ac, X = O



5 R^1 = R^2 = H
6 R^1 = R^2 = Ac
7 R^1 = Ac, R^2 = H



8 R = H
9 R = Ac



10 R = H
11 R = Ac

According to the physical and n.m.r. data reported, **1** was isolated[9] from the acid-catalysed reaction of D-glucose with urea but a pyranoid structure was assigned incorrectly. The chemical shifts for the resonances of C-4 and C-5 in **1** are δ 78.31 and 68.45, respectively (Table II), in good agreement with the ^{13}C-n.m.r. data of the analogous imidazolidin-2-one derivative[10].

Treatment of **1** with acetic anhydride–pyridine at 0° effected only *O*-acetylation and afforded **3**, as shown by the ^{1}H-n.m.r. data (Table III; 3 s at δ 2.105, 2.085, and 2.040, for 3 AcO). However, treatment of **1** with hot acetic anhydride–sodium acetate gave the *N*-acetyl-tri-*O*-acetyl derivative **4** as shown by the additional signal for NAc (s, δ 2.545). In accord with the furanoid structure, acetylation caused small downfield shifts (0.45 and 0.41 p.p.m., respectively) for the resonance of H-4 but significant shifts (1.38 and 1.39 p.p.m., respectively) for the resonance of H-5 in **3** and **4**. The ^{13}C-n.m.r data (Table IV) provided further proof for the structures of **3** and **4**, which were formulated incorrectly earlier[8].

TABLE I

^{1}H-N.m.r. data[a] for the cyclic carbamates

Compound	*Chemical shifts* (δ)							
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*
1	5.780d	4.939d	4.373s(b)	——3.85m——			3.706m	3.550m
5	5.264d	4.732dd	3.886dd	3.534t	3.344ddd		3.787dd	3.613dd
8	5.788d	4.967dd	4.414dd	3.948t	3.625m		3.654dd	3.540dd
10	5.684d	5.017t	4.190dd	3.729dd	3.792ddd		3.631dd	3.570m
12	5.770d	4.890d	4.288d	3.985m	3.782dd	3.667dd		
14	5.707d	5.029t	4.086dd	3.787ddd	3.866dd	3.659dd		
16	5.811d	4.970d	4.329s	4.057m	3.599dd	3.493dd		
18	5.453d	4.848dd	3.858dd	3.789ddd	3.930dd	3.479dd		
20	5.611d	5.056t	4.509t	4.115m	3.736dd	3.536dd		

	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
1	5.4	~0	~0	8.7			2.3	5.4	−12.1
5	3.3	4.7	9.6	9.4			2.5	6.2	−12.3
8	5.8	1.0	3.1	5.2			4.0	7.9	−12.5
10	5.4	5.5	9.2	2.9			4.8	7.4	−11.6
12	5.4	~0	2.7	4.3	7.3	−11.9			
14	5.4	5.5	9.3	2.2	4.7	−12.6			
16	5.6	~0	~0	4.6	6.9	−12.2			
18	5.3	3.3	8.1	5.1	3.9	−13.1			
20	5.9	5.9	5.8	3.9	8.3	−12.3			

[a] Recorded at 300 MHz for solutions in D_2O.

TABLE II

^{13}C-N.m.r. data[a] for the cyclic carbamates

Compound	*Chemical shifts (p.p.m.)*						
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*NCOO*
1	86.37	85.21	72.85	78.31	68.45	63.58	160.23
5	81.31	79.53	70.56	67.12	75.32	60.96	160.96
8	87.03	86.97	75.82	85.72	70.93	62.98	159.97
10	85.70	77.66	70.46	79.90	69.46	63.24	160.63
12	86.12	85.53	73.13	79.63	59.23		160.13
14	85.56	78.30	70.09	80.00	59.74		160.66
16	87.16	86.86	75.09	86.45	61.57		159.83
18	81.18	78.52	70.47	68.15	64.90		160.83
20	85.80	80.92	70.47	80.47	60.66		160.33

[a] Recorded at 75.5 MHz for solutions in D_2O.

The reaction of D-mannose with potassium cyanate in the presence of sodium dihydrogen phosphate gave two main products in almost equal ratio, namely, the *gluco* derivative **1** and β-D-mannopyranosylamine 1,2-(cyclic carbamate) (**5**). Thus, some 2-epimerisation had occured during the reaction. When ammonium chloride was the buffer, only 2% of **1** was isolated together with 33% of **5**. The $^4C_1$ conformation of the pyranoid ring in **5** was indicated by the large values of $J_{2,3}$ and $J_{4,5}$ in the ^{1}H-n.m.r. spectrum (Table I).

Further evidence for the pyranoid structure of **5** was provided by the large downfield shift (1.76 p.p.m.) of the signal of H-4 and the small shift (0.46 p.p.m.) of that of H-5 on conversion into the tetra-acetyl derivative **6** by treatment with hot acetic anhydride–sodium acetate. With acetic anhydride–pyridine at room temperature, **5** gave the triacetate **7**.

D-Galactose also furnished two products on reaction with potassium cyanate when sodium dihydrogen phosphate was used as a buffer, namely, the expected α-D-galactofuranosylamine 1,2-(cyclic carbamate) (**8**) but also the D-*talo* epimer **10**. Compound **10** was also obtained from D-talose under the above conditions of reaction. In the presence of ammonium chloride, D-galactose furnished only **8** (45%).

The ^{1}H-n.m.r. spectra of the respective tetra-acetyl derivatives **9** and **11** of **8** and **10** contained signals (4 s) for NAc and three OAc.

D-Xylose, D-ribose, and L-arabinose reacted with potassium cyanate to give the furanoid cyclic carbamates **12**, **14**, and **16**, respectively, and thence the corresponding triacetates **13**, **15**, and **17**. The ^{1}H- and ^{13}C-n.m.r. spectra of **12** and **13** accorded with reported data[11], except that the resonances of C-2 and C-4 in **12** were assigned incorrectly; the chemical shift of the resonance of C-2 (δ 85.53) is higher than that of C-4 (δ 79.63) as in **1** (Table II).

The structures of the D-*ribo* (**14** and **15**) and L-*arabino* (**16** and **17**) compounds were also characterised by their ^{1}H- and ^{13}C-n.m.r. spectra (Tables I–IV). On the basis of

TABLE III

^{1}H-N.m.r. data[a] for the acetylated derivatives of cyclic carbamates

Compound	*Chemical shifts* (δ)									
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*	*Others*	
									NH/NAc	*OAc*
3	5.813d	4.892d	5.517d	4.300dd	5.233ddd		4.548dd	4.088dd	6.267	2.105,2.085,2.040
4	6.337d	4.833d	5.554d	4.262dd	5.242ddd		4.580dd	4.066dd	2.545	2.104,2.054,2.015
6	5.934d	4.792dd	5.235dd	5.291dd	3.808tdd		4.092dd	4.326dd	2.530	2.135,2.079,2.064
7	5.226d	4.844t	5.206dd	5.268t(b)	3.715m		4.155dd	4.247dd	6.300	2.129,2.091,2.067
9	6.325d	4.939d	5.205d	4.381dd	5.316m		4.242dd	4.136dd	2.568	2.152,2.124,2.051
11	6.270d	5.156t	4.816dd	4.181dd	5.251ddd		4.302dd	4.251dd	2.545	2.155,2.122,2.053
13	6.323d	4.877d	5.466d	4.364m	4.314dd	4.228dd			2.547	2.184, 2.080
15[b]	5.633d	4.413t	4.500dd	3.783ddd	4.151dd	3.946dd			2.195	1.585(2)
17	6.311d	4.958d	5.264d	4.379m	4.362dd	4.078dd			2.533	2.146, 2.091
19	6.084d	4.882d	5.282dd	5.127ddd	4.055dd	3.724dd			2.556	2.161, 2.096
21	6.157d	5.139t	5.362t	4.518m	4.358dd	4.091dd			2.549	2.161, 2.075

	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
3	5.3	~0	2.8	9.2			2.4	5.2	−12.3
4	5.3	~0	2.9	9.0			2.7	5.4	−12.3
6	3.3	4.1	9.6	8.9			2.5	4.8	−12.4
7	3.2	4.5	9.6	8.8			2.8	5.4	−12.3
9	5.9	~0	1.5	4.3			4.8	6.8	−11.8
11	5.5	5.4	9.1	3.1			4.7	6.3	−12.0
13	5.4	~0	2.9	5.1	6.1	−11.2			
15[b]	5.5	5.3	9.2	2.7	5.0	−12.4			
17	5.8	~0	1.7	4.5	5.3	−13.9			
19	5.8	3.1	7.9	5.3	2.8	−13.9			
21	6.0	5.9	6.9	6.3	3.9	−12.4			

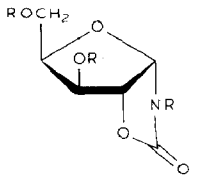
[a] Recorded at 300 MHz for solutions in $CDCl_3$ except where noted. [b] In C_6D_6.

TABLE IV

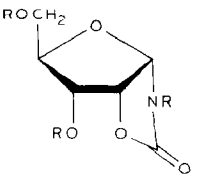
^{13}C-N.m.r. data[a] for the acetylated derivatives of cyclic carbamates

Compound	*Chemical shifts (p.p.m.)*							
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*NCOO*	*Others*
3	86.00	82.87	75.62	73.39	67.11	62.94	156.90	170.66, 169.67, 169.21 (COO) 20.64 (2), 20.49 (*Me*COO)
4	86.00	79.68	76.70	72.95	66.99	62.66	151.72	170.38, 169.41, 169.19, 169.08 (COO, CON) 23.51 (*Me*CON), 20.54(2), 20.40 (*Me*COO)
6	79.86	73.11[b]	72.17[b]	69.24[b]	61.95[b]	61.62	151.80	170.50, 170.04, 169.07, 168.66 (COO, CON) 23.51 (*Me*CON), 20.55, 20.42, 20.40 (*Me*COO)
7	80.93	75.05[b]	72.03[b]	69.52[b]	65.51[b]	62.19	157.47	170.66, 170.27, 169.19 (COO) 20.68, 20.56(2) (*Me*COO)
9	87.13	84.76	77.64	80.82	69.67	62.33	151.58	170.30, 170.13, 169.52(2) (COO, CON) 23.51 (*Me*CON), 20.49(2), 20.31 (*Me*COO)
11	85.19	75.71	71.09	73.60	68.06	62.39	152.10	170.41, 169.94, 169.79, 169.27 (COO, CON) 23.53 (*Me*CON), 20.60, 20.53, 20.16 (*Me*COO)
13	85.69	79.80	76.47	74.16	60.41		151.69	170.27, 169.51, 169.20 (COO, CON) 23.55 (*Me*CON), 20.57, 20.42 (*Me*COO)
15	85.24	75.09	71.49	73.82	61.36		152.16	170.39, 169.92, 169.56 (COO, CON) 24.79 (*Me*CON), 20.57, 20.42 (*Me*COO)
17	86.90	83.69	77.39	81.12	63.34		151.61	170.44, 169.60, 169.49 (COO, CON) 23.46 (*Me*CON), 20.49, 20.27 (*Me*COO)
19	80.06	71.97[c]	69.03[b]	68.33[b]	63.73		152.24	170.11 (2), 169.15 (COO, CON) 23.53 (*Me*CON), 20.70(2) (*Me*COO)
21	85.16	74.36[c]	71.10	76.98[c]	61.66		151.92	170.40, 169.62(2) (COO, CON) 23.49 (*Me*CON), 20.44, 20.12 (*Me*COO)

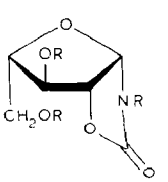
[a] Recorded at 75.5 MHz for solutions in $CDCl_3$. [b] Assignments may have to be reversed.



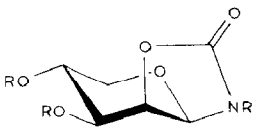
12 R = H
13 R = Ac



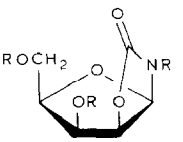
14 R = H
15 R = Ac



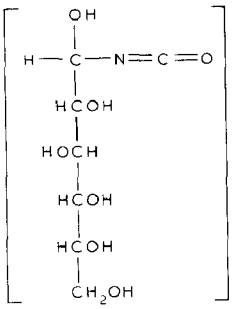
16 R = H
17 R = Ac



18 R = H
19 R = Ac



20 R = H
21 R = Ac



22

the physical data, the ribose derivative **14** is identical with the compound described by Pithová *et al.*[12]. The structure of **14** has been corroborated by X-ray crystallography[13]. The characteristics of the L-arabinose derivatives **16** and **17** correspond well with those of the D enantiomers[14].

The reaction of D-lyxose with potassium cyanate (1.5 mol) gave a complex mixture even in buffered solutions. In the presence of ammonium chloride (1.5 mol), three cyclic carbamates were isolated, namely, the D-xylose derivative **12** (3%), formed by 2-epimerisation, the D-lyxopyranose derivative **18** (22%), and the D-lyxofuranose derivative **20** (6%). When sodium dihydrogen phosphate was used as a buffer in the usual ratio (0.55 mol), a multicomponent mixture of products was obtained. However, if the molar ratio of the phosphate was increased to 1.5, **18** was almost the sole product and could be isolated by crystallisation in a yield of 36%

The structures of **18** and **20** and the respective triacetates **19** and **21**, were established by ^{1}H- and ^{13}C-n.m.r. spectroscopy (Tables I–IV). The resonance of H-4 was shifted downfield by 1.34 p.p.m. in the conversion **18**→**19** (pyranoid system), but only by 0.40 p.p.m. in the conversion **20**→**21** (furanoid system). The signal for C-1 exhibited a markedly lower chemical shift in the pyranosyl (**5**–**7**, **18**, and **19**) than in the furanosyl cyclic carbamates (**1**, **3**, **4**, **8**–**17**, **20**, and **21**), in accord with the ^{13}C-n.m.r. data[15] of aldopyranoses, aldofuranoses, and their acetylated derivatives, the spectral data[15] of which were the basis for ^{13}C assignments in Tables II and IV.

The fact that D-mannose and D-lyxose form pyranosyl 1,2-cyclic carbamates can be attributed to the steric interaction of the 3,4-substituents with the oxazolidine ring in the furanoid structure. The large values of $J_{1,2}$ in the lyxopyranose derivatives (5.3 and 5.8 Hz in **18** and **19**, respectively) suggest significant flattening of the pyranoid ring, which was proved by X-ray diffraction studies[16] of **18**.

The formation of the 1,2-cyclic carbamates of glycosylamines appears to involve acyclic isocyanate intermediates (*e.g.*, **22**), which then undergo intramolecular reactions with HO-2 to give the oxazolidine moiety. Ring closure to give furanosyl or pyranosyl products could involve either simultaneous or consecutive equilibrium processes. Studies of the reaction mechanism including the epimerisation are in progress.

EXPERIMENTAL

General. — T.l.c. was performed on Silica Gel F_{254} (Merck) with *A*, ethyl acetate–ethanol–water (7:2:1); *B*, chloroform–acetone (95:5); and *C*, *tert*-butyl methyl ether–light petroleum (9:1); and detection by charring with sulfuric acid. Silica gel (230–400 mesh) was used for column chromatography. Melting points were determined on a Leitz SM Lux microscope. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter and i.r. spectra with a Zeiss Specord 75IR spectrometer. A Bruker AM 300 spectrometer was used to obtain ^{1}H- (solutions in D_2O, internal HOD 4.78 p.p.m.; solutions in $CDCl_3$, internal Me_4Si) and ^{13}C-n.m.r. spectra (solutions in D_2O, internal acetone δ 30.5; solutions in $CDCl_3$, internal Me_4Si). The δ and J values for ^{1}H resonances were calculated as first-order spectra at 300 MHz. The chemical shifts for the resonances of ring carbons were assigned by comparison with the ^{13}C-n.m.r. data[15] for aldoses, methyl aldosides, and their acetylated derivatives.

Aldosylamine 1,2-(cyclic carbamates). — (*a*) To a solution of the aldose (7.5 mmol) in water (5 mL) were added potassium cyanate (0.93 g, 11.5 mmol) and sodium dihydrogen phosphate (0.50 g, 4.2 mmol). The mixture was heated at 60° for 6 h (pH 7→9), then concentrated together with silica gel 60 (5 g), and toluene was repeatedly evaporated from the residue which was then eluted[17] from a short column (30 × 70 mm) of Silica Gel 60 with solvent *A* (18 mL).

(*b*) To a solution of the aldose (9 mmol) in water (6 mL) were added potassium cyanate (1.09 g, 13.5 mmol) and ammonium chloride (0.72 g, 13.5 mmol). The mixture was heated at 60° for 6 h (pH 7→8.5), then worked-up as in (*a*).

Acetylation of the cyclic carbamates. — (*a*) The di- and tri-*O*-acetyl derivatives were prepared by conventional treatment of the cyclic carbamates with acetic anhydride–pyridine.

(*b*) The *N*-acetyl-di- and -tri-*O*-acetyl derivatives were prepared as follows. A mixture of the cyclic carbamate (2 mmol) and anhydrous sodium acetate (0.50 g, 6 mmol) in acetic anhydride (5 mL) was boiled under reflux for 1 h, then poured into ice–water (50 mL), and extracted with chloroform. The extract was concentrated, a solution of the residue in ethanol was clarified with charcoal, then concentrated, and toluene was evaporated repeatedly from the residue.

α-D-Glucofuranosylamine 1,2-(cyclic carbamate) (**1**, α-D-glucofurano[1,2-*d*]oxazolidin-2-one). — D-Glucose (1.35 g, 7.5 mmol) was reacted by general procedure (*a*). T.l.c. revealed one main product, R_t 0.65 (solvent *A*) and D-glucose (R_t 0.2). Chromatography (solvent *A*) of the mixture gave **1** (0.52 g, 34%), m.p. 181–184° (from ethanol), $[\alpha]_D$ +6.6° (*c* 3, water) {lit.[8] $[\alpha]_D$ +6.79° (water); lit.[9] m.p. 186–187°, $[\alpha]_D$ +6.1° (*c* 0.95,

water)}; ν_{max}^{KBr} 1730 cm^{-1} (CO). Compound **1** was identical with "μ-hydroxyglucoxazolin" prepared according to the procedure reported[8].

(*b*) D-Glucose (1.62 g, 9 mmol), when treated by the general procedure (*b*), gave **1** (0.55 g, 30%), m.p. 181–184° (from ethanol).

The triacetate (**3**, 57%) of **1** had R_F 0.2 (solvent *B*), m.p. 109–111° (from water), $[\alpha]_D$ +63° (*c* 2.2, chloroform) {lit.[8] m.p. 139°, $[\alpha]_D$ +58.86° (chloroform)}; ν_{max}^{KBr} 3400 (NH), 1780–1720 cm^{-1} (carbamate CO, Ac).

Anal. Calc. for $C_{13}H_{17}NO_9$: C, 47.13; H, 5.17; N, 4.23. Found: C, 47.01; H, 5.31; N, 4.09.

The tetra-acetyl derivative (**4**, 83%) of **1** had R_F 0.4 (solvent *B*), R_F 0.7 (solvent *C*), m.p. 93–95° (from ethanol), $[\alpha]_D$ +109° (*c* 1, chloroform) {lit.[8] m.p. 95°, $[\alpha]_D$ +104.8° (chloroform)} ν_{max}^{KBr} 1800 (carbamate CO), 1760 (OAc), 1730 cm^{-1} (NAc).

Reaction of D-*mannose with potassium cyanate.* — (*a*) Reaction of D-mannose (1.35 g, 7.5 mmol) by the general procedure (*a*) gave (t.l.c.) a mixture of two main products with R_F 0.65 and 0.4, together with D-mannose, R_F 0.3 (solvent *A*). Column chromatography (solvent *A*) of the mixture afforded, first, **1** (348 mg, 23%) and then β-D-mannopyranosylamine 1,2-(cyclic carbamate) (**5**, β-D-mannopyrano[1,2-*d*]oxazolidin-2-one) (328 mg, 21%) R_F 0.4 (solvent *A*), m.p. 176–179° (from ethanol), $[\alpha]_D$ −40° (*c* 2.1, water); ν_{max}^{KBr} 1710 cm^{-1} (CO).

Anal. Calc. for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 41.07; H, 5.60; N, 6.69.

(*b*) Treatment of D-mannose (1.62 g, 9 mmol) by the general procedure (*b*), with column chromatography (solvent *A*) of the product, yielded, first, **1** (45 mg, 2%) and then **5** (605 mg, 33%).

The tetra-acetyl derivative (**6**, 67%) of **5** had R_F 0.25 (solvent *B*), m.p. 133–134° (from ethanol), $[\alpha]_D$ −105° (*c* 1, chloroform); ν_{max}^{KBr} 1790 (carbamate CO), 1720 (OAc), 1710 cm^{-1} (NAc).

Anal. Calc. for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.45; H, 5.53; N, 3.49.

The triacetate (**7**, 82%) of **5** had R_F 0.1 (solvent *B*), m.p. 203° (from ethanol), $[\alpha]_D$ −66° (*c* 1, chloroform); ν_{max}^{KBr} 3260 (NH), 1730 cm^{-1} (carbamate CO, Ac).

Anal. Calc. for $C_{13}H_{17}NO_9$: C, 47.13; H, 5.17; N, 4.23. Found: C, 47.07; H, 5.25; N, 4.50.

Reaction of D-*galactose with potassium cyanate.* — (*a*) D-Galactose (1.35 g, 7.5 mmol), when treated by the general procedure (*a*), gave (t.l.c.) two main products (R_F 0.6 and 0.4), several by-products, and D-galactose, R_F 0.35–0.25 (solvent *A*). Column chromatography (solvent *A*) of the mixture afforded, first, α-D-galactofuranosylamine 1,2-(cyclic carbamate) (**8**, α-D-galactofurano[1,2-*d*]oxazolidin-2-one), as a syrup (315 mg, 20.5%), R_F 0.6 (solvent *A*), $[\alpha]_D$ +7° (*c* 2.8, methanol); ν_{max}^{film} 1720 cm^{-1} (CO).

Anal. Calc. for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 41.15; H, 5.61; N, 6.60.

Eluted second was β-D-talofuranosylamine 1,2-(cyclic carbamate) (**10**, β-D-talofurano[1,2-*d*]oxazolidin-2-one) (209 mg, 14%), R_F 0.4 (solvent *A*), m.p. 134° (from ethanol), $[\alpha]_D$ −103° (*c* 1, methanol); ν_{max}^{KBr} 1700 cm^{-1} (CO).

Anal. Found: C, 41.06; H, 5.58; N, 6.59.

When D-talose (1.08 g, 6 mmol) was reacted by the general procedure (*a*), the main product was **10** (455 mg, 31%), R_f 0.4 (solvent *A*), m.p. 134° (from ethanol), identical with the product described above.

(*b*) D-Galactose (1.62 g, 9 mmol), when treated according to the general procedure (*b*), gave (t.l.c.) a mixture of one main product (R_f 0.6, solvent *A*) and D-galactose. The usual processing of the mixture gave **8** as a syrup (839 mg, 45%), identical with the main product from (*a*).

The tetra-acetyl derivative (**9**, 61%) of **8** was a syrup, R_f 0.35 (solvent *B*), $[\alpha]_D$ +70° (*c* 2, chloroform); $\nu_{max}^{CHCl_3}$ 1790 (carbamate CO), 1740 cm^{-1} (Ac).

Anal. Calc. for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.41; H, 5.40; N, 3.57.

The tetra-acetyl derivative (**11**, 71%) of **10** was a syrup, R_f 0.25 (solvent *B*), $[\alpha]_D$ −182° (*c* 1.2, chloroform); $\nu_{max}^{CHCl_3}$ 1790 (carbamate CO), 1730 cm^{-1} (Ac).

Anal. Found: C, 48.39; H, 5.37; N, 3.60.

α-D-Xylofuranosylamine 1,2-(cyclic carbamate) (**12**, α-D-xylofurano[1,2-*d*]oxazolidin-2-one). — D-Xylose (1.35 g, 9 mmol) was reacted according to general procedure (*b*). Chromatography (solvent *A*) of the product gave **12** (1.19 g, 75%), R_f 0.7 (solvent *A*), m.p. 126–129° (from nitromethane), $[\alpha]_D$ −4° (*c* 4, water) (the compound was described previously[11] as a syrup), ν_{max}^{KBr} 1740 cm^{-1} (CO).

Anal. Calc. for $C_6H_9NO_5$: C, 41.15; H, 5.18; N, 8.00. Found: C, 40.88; H, 4.86; N, 8.09.

The triacetyl derivative (**13**, 67%) of **12** had m.p. 160–162°, $[\alpha]_D$ +80° (*c* 2.3, chloroform) (described previously[11] as a syrup); ν_{max}^{KBr} 1780 (carbamate CO), 1730 (OAc), 1710 cm^{-1} (NAc).

Anal. Calc. for $C_{12}H_{15}NO_8$: C, 47.84; H, 5.02; N, 4.65. Found: C, 47.65; H, 4.82; N, 4.79.

α-D-Ribofuranosylamine 1,2-(cyclic carbamate) (**14**, α-D-ribofurano[1,2-*d*]oxazolidin-2-one). — Reaction of D-ribose (1.35 g, 9 mmol) by the general procedure (*b*), with chromatography (solvent *A*) of the product, furnished **14** (39%), R_f 0.6 (solvent *A*), m.p. 161–164° (from ethanol), $[\alpha]_D$ +106° (*c* 1.9, methanol) (lit.[12] m.p. 169–170°); ν_{max}^{KBr} 1730 cm^{-1} (CO).

Anal. Calc. for $C_6H_9NO_5$: C, 41.15; H, 5.18; N, 8.00. Found: C, 40.97; H, 4.86; N, 8.03.

The triacetyl derivative (**15**, 76%) of **14** was a syrup, R_f 0.35 (solvent *B*), $[\alpha]_D$ +127° (*c* 1.5, chloroform); $\nu_{max}^{CHCl_3}$ 1785 (carbamate CO), 1730 cm^{-1} (Ac).

Anal. Calc. for $C_{12}H_{15}NO_8$: C, 47.84; H, 5.02; N, 4.65. Found: C, 47.72; H, 4.97; N, 4.60.

β-L-Arabinofuranosylamine 1,2-(cyclic carbamate) (**16**, β-L-arabinofurano[1,2-*d*]oxazolidin-2-one). — Treatment of L-arabinose (1.35 g, 9 mmol) by the general procedure (*b*), with chromatography (solvent *A*) of the product, gave **16** (66%), R_f 0.7 (solvent *A*), m.p. 118–121° (from nitromethane), $[\alpha]_D$ +39° (*c* 1.6, pyridine) {lit.[14] for the syrupy D enantiomer, $[\alpha]_D$ −35.7° (pyridine)}; ν_{max}^{KBr} 1740 cm^{-1} (CO).

Anal. Calc. for $C_6H_9NO_5$: C, 41.15; H, 5.18; N, 8.00. Found: C, 40.98; H, 4.91; N, 8.03.

The triacetyl derivative (**17**, 71%) of **16** had R_F 0.35 (solvent *B*), m.p. 75°, $[\alpha]_D$ +104° (*c* 2, chloroform) {lit.[14] for the D enantiomer, m.p. 80–81°, $[\alpha]_D$ −109° (chloroform)}; $\nu_{max}^{CHCl_3}$ 1790 (carbamate CO), 1730 (OAc), 1720 cm^{-1} (NAc).

Anal. Calc. for $C_{12}H_{15}NO_8$: C, 47.84; H, 5.02; N, 4.65. Found: C, 48.11; H, 5.25; N, 4.48.

Reaction of D-*lyxose with potassium cyanate.* — (*a*) Reaction of D-lyxose (1.35 g, 9 mmol) by the general procedure (*b*) gave (t.l.c.) a complex mixture that contained products with R_F 0.7, 0.6, and 0.5, together with D-lyxose, R_F <0.4 (solvent *A*). Column chromatography (ethyl acetate–ethanol, 4:1) of the mixture gave, first, **12** (47 mg, 3%), R_F 0.7 (solvent *A*), m.p. 126–128° (from ethanol), identical with the product described above.

Eluted second was β-D-lyxopyranosylamine 1,2-(cyclic carbamate) (**18**, β-D-lyxopyrano[1,2-*d*]oxazolidin-2-one) (346 mg, 22%), R_F 0.6 (solvent *A*), m.p. 148–150° (from ethanol), $[\alpha]_D$ −120° (*c* 1.1, water); ν_{max}^{KBr} 1720 cm^{-1} (CO).

Anal. Calc. for $C_6H_9NO_5$: C, 41.15; H, 5.18; N, 8.00. Found: C, 41.02; H, 5.50; N, 7.89.

Eluted third was syrupy β-D-lyxofuranosylamine 1,2-(cyclic carbamate) (**20**, β-D-lyxofurano[1,2-*d*]oxazolidin-2-one) (91 mg, 6%), R_F 0.5 (solvent *A*), $[\alpha]_D$ −39° (*c* 2.5, water); ν_{max}^{MeOH} 1750 cm^{-1} (CO).

Anal. Found: C, 41.26; H, 5.32; N, 7.77.

(*b*) Reaction of D-lyxose (1.35 g, 9 mmol) by the general procedure (*a*), but using more sodium dihydrogen phosphate (1.62 g, 13.5 mmol) and reaction for 1.5 h (pH 6.5 → 7.5), gave **18** (0.71 g, 45%), R_F 0.6 (solvent *A*), slightly contaminated with **12** and **20** (R_F 0.7 and 0.5, respectively). Recrystallisation from ethanol gave **18** (0.57 g, 36%), m.p. 148–150°.

The triacetyl derivative (**19**, 81%) of **18** was a syrup, R_F 0.4 (solvent *B*), $[\alpha]_D$ −164° (*c* 2, chloroform); $\nu_{max}^{CHCl_3}$ 1790 (carbamate CO), 1730 cm^{-1} (Ac).

Anal. Calc. for $C_{12}H_{15}NO_8$: C, 47.84; H, 5.02; N, 4.65. Found: C, 48.01; H, 5.21; N, 4.44.

The triacetyl derivative (**21**, 75%) of **20** was a syrup, R_F 0.2 (solvent *B*), $[\alpha]_D$ −150° (*c* 0.9, chloroform); $\nu_{max}^{CHCl_3}$ 1790 (carbamate CO), 1730 cm^{-1} (Ac).

Anal. Found: C, 48.05; H, 5.27; N, 4.48.

ACKNOWLEDGMENTS

We thank Mrs. M. Rundshagen and Mr. D. Neemeyer for performing the n.m.r. spectra, and Professor A. Messmer for his interest.

REFERENCES

1 Y. Takagi, C. Komuro, T. Tsuchiya, and S. Umezawa, *Bull. Chem. Soc. Jpn.*, 54 (1981) 1834–1837, and references therein.
2 H. D. Tresner, J. H. Korshalla, A. A. Fantini, J. D. Korshalla, J. P. Kirby, J. J. Goodman, R. A. Kele, A. J. Shay, and D. B. Borders, *J. Antibiot.*, 31 (1978) 394–397.
3 G. A. Ellestad, D. B. Cosulich, R. W. Broschard, J. H. Martin, M. P. Kunstmann, G. O. Morton, J. E. Lancaster, W. Fulmor, and F. M. Lovell, *J. Am. Chem. Soc.*, 100 (1978) 2515–2524.
4 J. Kovács, I. Pintér, A. Messmer, and G. Tóth, *Carbohydr. Res.*, 141 (1985) 57–65.
5 J. Kovács, I. Pintér, A. Messmer, G. Tóth, and H. Duddeck, *Carbohydr. Res.*, 166 (1987) 101–111.
6 J. C. Jochims, A. Seeliger, and G. Taigel, *Chem. Ber.*, 100 (1967) 845–854.
7 J. Kovács, I. Pintér, A. Messmer, G. Tóth, U. Lendering, and P. Köll, *Carbohydr. Res.*, 198 (1990) 358–362.
8 G. Zemplén, Á. Gerecs, and M. Rados, *Ber.*, 69 (1936) 748–754.
9 R. F. Helm and J. J. Karchesy, *J. Carbohydr. Chem.*, 8 (1989) 687–692.
10 J. A. Galbis Pérez, F. Zamora Mata, and P. Turmo Fernández, *Carbohydr. Res.*, 163 (1987) 132–135.
11 L. Benzing-Purdie and J. H. Nikiforuk, *J. Carbohydr. Chem.*, 2 (1983) 439–447.
12 P. Pithová, A. Pískala, J. Pitha, and F. Šorm, *Collect. Czech. Chem. Commun.*, 30 (1965) 2801–2811.
13 P. Singh and D. J. Hodgson, *Acta Crystallogr., Sect. B*, 32 (1976) 2329–2333.
14 M. Merész, Gy. Horváth, P. Sohár, and J. Kuszmann, *Tetrahedron*, 31 (1975) 1873–1877.
15 K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.*, 41 (1983) 27–66.
16 J. Kopf, J. Kovács, and P. Koll, *Acta Crystallogr., Sect. C*, submitted.
17 L. M. Harwood, *Aldrichimica Acta*, 18 (1985) 25.