Carbohydrate Research, 166 (1987) 101–111
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A NEW ROUTE TO CYCLIC UREA DERIVATIVES OF SUGARS *via* PHOSPHINIMINES

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(Received February 3rd, 1987; accepted for publication, March 11th, 1987)

ABSTRACT

Sugar phosphinimines and the corresponding aminophosphonium salts were prepared from 2-amino-2-deoxy-D-glucosyl azide derivatives and their structures were established by ^{13}C- and ^{31}P-n.m.r. spectroscopy. A simple one-pot procedure, involving reaction of the azides with triphenylphosphine and carbon dioxide, provides an efficient access to cyclic urea derivatives.

INTRODUCTION

Protected sugar phosphinimines react with carbon dioxide to give carbodiimides[1], but the reaction with unprotected phosphinimines leads to cyclic carbamates[2]. In order to find a simple synthesis of the corresponding cyclic urea derivatives, which have significance as potential components of aminoglycoside antibiotics[3,4], sugar phosphinimines having an adjacent amino function have been prepared.

RESULTS AND DISCUSSION

The Staudinger reaction[5] of the 2-acetamido- and 2-amino-2-deoxyglucosyl azides[6–8] **1–3** with triphenylphosphine yielded the corresponding phosphinimines **4–6**. Compound **4** was a stable crystalline solid and **5**, which was non-crystalline, was reasonably stable in dry solvents. In contrast, **6** was unstable and its structure could be investigated only when the compound was prepared *in situ* in dry *N,N*-dimethylformamide. Treatment of **4** with perchloric acid afforded the expected

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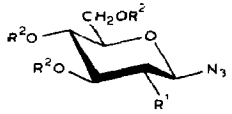
0008-6215/87/$ 03.50



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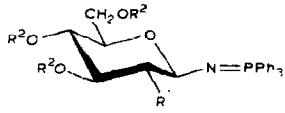
2 R^1 = NH_2, R^2 = Ac
3 R^1 = NH_2, R^2 = H



4 R^1 = NHAc, R^2 = Ac
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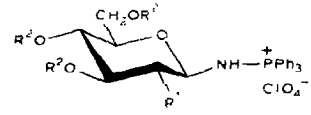


7 R^1 = NHAc, R^2 = Ac
8 R^1 = NH_3^+ ClO_4^-, R^2 = Ac
9 R^1 = NH_3^+ ClO_4^- R^2 = H

aminophosphonium salt **7**, but **5** and **6** gave the corresponding bis(perchlorate) salts **8** and **9**, due to the presence of the 2-amino group.

The structure of the new compounds was established by ^{13}C- and ^{31}P-n.m.r. spectroscopy (Table I) which revealed characteristic differences between the phosphinimines **4–6** and the aminophosphonium salts **7–9**, particularly in the chemical shifts of the signals for phosphorus and of those for C-1 and C-ipso, in agreement with earlier results[2]. The phosphinimines **4–6** had large $^3J_{P,C\text{-}2}$ values (21.3–22.7 Hz) indicating the *γ-anti* orientation of P–N and C-1–C-2 bonds[2] stabilised by the exo-anomeric effect.

TABLE I

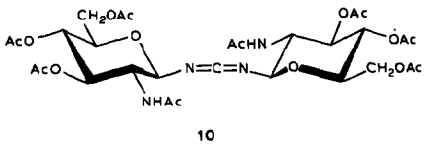
^{13}C- AND ^{31}P-N.M.R. DATA[a] FOR **4–9**

Compound	*Chemical shifts (δ scale)*[b]						
	C-1	*C-2*	*C-ipso*	*C-ortho*	*C-meta*	*C-para*	*P*
4[c]	89.9	58.0	131.9	133.0	128.3	131.8	16.28
	(3)	(22.0)	(97.4)	(9.5)	(11.7)		
5[c]	92.5	60.4	131.7	133.0	128.7	132.0	15.02
	(<2)	(22.7)	(97)	(9.5)	(11.7)		
6[c]	91.4	61.7	132.1	133.6	128.7	131.7	13.38
	(5)	(21.3)	(97.0)	(9.5)	(11.7)		
7[d]	82.4	55.6	119.5	133.9	130.1	135.5	40.32
	(~2)	(~12)	(103)	(11.0)	(13.9)		
8[d]	80.8	54.9	118.6	134.1	130.1	135.8	42.47
	(~3)	(~12)	(102.6)	(10.3)	(12.5)		
9[c]	80.6	55.5	119.1	129.2	133.4	134.7	40.60
	(3)	(9.5)	(102.6)	(13.2)	(11.7)		

[a]Recorded at 25 MHz (^{13}C) and 40 MHz (^{31}P), respectively. [b]Couplings (Hz) of ^{31}P with the corresponding ^{13}C in parentheses. [c]In $(CD_3)_2NCDO$. [d]In $CDCl_3$.

Reaction of **1** with triphenylphosphine–carbon dioxide under mild conditions gave the symmetrical carbodi-imide **10**, as for protected sugar phosphinimines[1]. Compound **10**, the carbodi-imide structure of which was proved by the i.r. absorption at 2150 cm^{-1} and the ^1H- and ^{13}C-n.m.r. data, could be converted readily into the symmetrical urea derivative **11**.

In contrast to **1**, 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl



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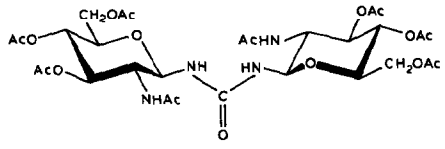
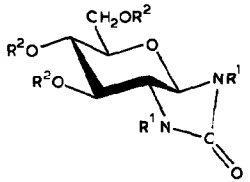


11

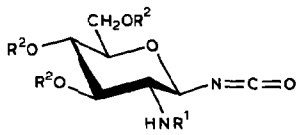
azide (**2**) reacted with triphenylphosphine–carbon dioxide to afford 3,4,6-tri-*O*-acetyl-1,2-(carbonyldi-imino)-1,2-dideoxy-β-D-glucopyranose (**12**) in good yield with or without isolation of **5**. Compound **12** had no i.r. absorption for carbodi-imide but a broad carbonyl absorption, and the ^{13}C-n.m.r. spectrum revealed a characteristic signal for the urea carbonyl carbon at δ 162.1 p.p.m. *trans*-Diequatorial fusion of the imidazolidone and pyranoid rings was proved by the large $J_{1,2}$ value (~9 Hz). Similarly, 2-amino-2-deoxy-β-D-glucopyranosyl azide (**3**) could be converted in almost quantitative yield into the cyclic urea **13**, which had a strong i.r. band for carbonyl at 1690 cm^{-1} and an n.m.r. signal for a urea carbonyl carbon at δ 162.3. Treatment of **13** with acetic anhydride–pyridine gave the triacetate **12** which, with acetic anhydride–trifluoroacetic acid[9], gave the di-*N*-acetyl derivative **14**, the ^{1}H-n.m.r. spectrum of which contained two additional signals for NAc groups (δ 2.47 and 2.52).

The formation of cyclic ureas and carbodi-imides involves glycosyl isocyanate intermediates (**15**–**17**). Cyclisation of **16** and **17** involves the vicinal amino group and leads to **12** and **13**, respectively, whereas **15**, which has a vicinal acetamido group, reacts with another phosphinimine molecule to give the carbodi-imide **10**.

The reaction of glycosyl azides with triphenylphosphine and carbon dioxide to afford cyclic ureas is not limited to 2-amino-2-deoxy-β-D-glucopyranosyl azides. Thus, methyl 3-amino-2-azido-2,3-dideoxy-α-D-altroside (**18**), prepared *in situ* by reaction of its hydrochloride[10] with sodium methoxide, furnished the cyclic urea **19**, which had ν_{max} at 1680 cm^{-1} and exhibited a singlet at δ 167.9 in the ^{13}C-n.m.r. spectrum (Table III). Because of the *trans*-diaxial orientation of the azido and amino groups ($J_{1,2}$ 3.3, $J_{2,3}$ 5.3 Hz for **18**·HCl) (Table II), $^4C_1$ to $^1C_4$ inversion was required for the cyclisation. The *trans*-diequatorial fusion of the imidazolidone and pyranoid rings in **19** was indicated by the large $J_{2,3}$ value (12.4 Hz) (Table II) of its



12 R^1 = H, R^2 = Ac
13 R^1 = R^2 = H
14 R^1 = R^2 = Ac



15 R^1 = R^2 = Ac
16 R^1 = H, R^2 = Ac
17 R^1 = R^2 = H

TABLE II

^{1}H-N.M.R. DATA[a] FOR **18–21**

Compound	*Chemical shifts (δ scale)*								
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*OMe*	*Others*
18·HCl[b]	4.76	3.92	3.56	3.98	3.74	3.72	3.64	3.33	
19[b]	4.72		(3.52–3.67)	3.91	(3.52–3.67)	3.52	3.41	3.32	
20[c]	4.68	3.59	3.56	5.03	4.02	4.14	4.12	3.37	2.02, 2.04 (2 OAc)
21a[c]	5.99	4.55	4.75	5.54	5.07	4.17	4.29	3.39	2.10, 2.01, 1.98, 1.93 (4 OAc) 2.44, 2.42 (2 NAc)
21b[c]	5.96	4.48	4.71	5.44	5.17	4.27	4.33	3.34	2.10, 2.09, 2.01, 1.91 (4 OAc), 2.47, 2.44 (2 NAc)
	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$		
18·HCl	3.3	5.3	4.6	8.3	2.8	6.1	12.5		
19	6.9		~4.6	~4.6	7.0	4.4	13.0		
20	6.7	12.4	3.9	6.0	6.0	4.0	12.0		
21a	2.2	1.8	1.5	8.7	4.2	2.9	12.5		
21b	2.4	1.4	1.4	7.5	5.1	3.1	12.4		

[a]At 400 MHz. [b]In D_2O. [c]In $CDCl_3$.

TABLE III

^{13}C-N.M.R. DATA[a] FOR **18–21**

Compound	*Chemical shifts (p.p.m.)*							
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OMe*	*NCON*
18·HCl[b]	98.1	51.5	58.6	61.4	71.2	60.7	56.2	—
19[b]	102.6	54.8	56.3	64.1	77.6	62.1	55.8	167.9
20[c]	102.1	55.2	54.3	66.3	70.3	63.6	55.1	164.8
21a[c]	94.9	52.2	50.9	69.2	68.7	61.2	57.7	151.7
21b[c]	94.3	52.9	50.9	69.1	68.4	61.1	58.2	151.7

[a]At 100 MHz. [b]In D_2O. [c]In $CDCl_3$.

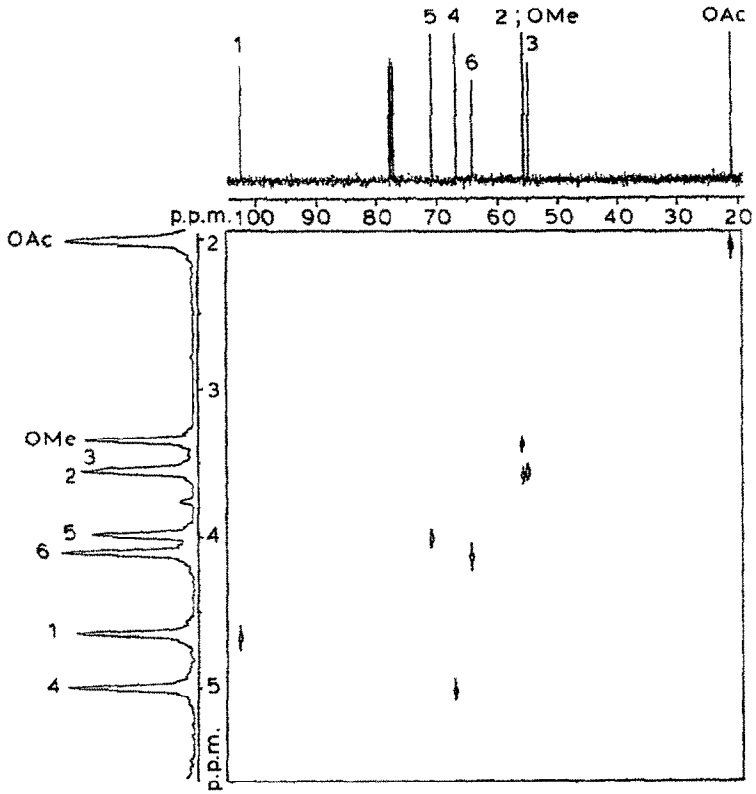


Fig. 1. ^{13}C-^{1}H correlated 2D-n.m.r. spectrum of **20** with the broad-band, proton-decoupled 1D ^{13}C spectrum (above) and the projection of the broad-band proton–proton decoupled ^{1}H spectrum (left).

diacetate **20** obtained by conventional acetylation of **19**. Unambiguous assignment of the signals for C-2,3 was permitted by the 2D ^{13}C–^{1}H chemical shift correlation map with the aid of the first-order 400-MHz ^{1}H-n.m.r. spectrum of **20** (Fig. 1).

Zemplén deacetylation of **20** regenerated **19**, which proved the presence of the same bicyclic structure in each molecule.

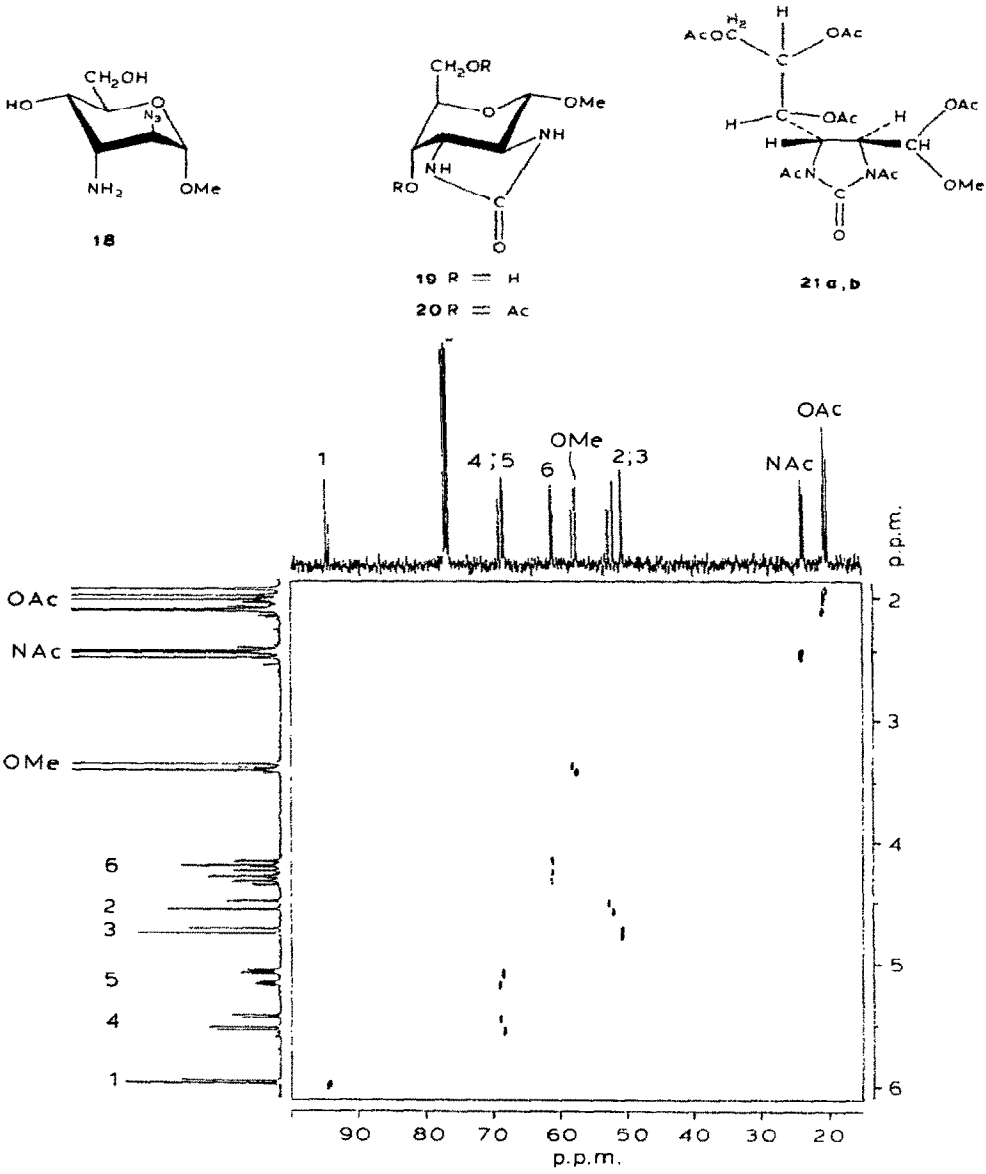


Fig. 2. ^{13}C–^{1}H correlated 2D-n.m.r. spectrum of the mixture of **21a** and **21b**. The traces on the top and on the left of the 2D spectrum are not the projections but the "normal" 1D ^{13}C- and ^{1}H-n.m.r. spectra.

Treatment of the diacetate **20** with acetic anhydride–trifluoroacetic acid gave a crystalline product which, on the basis of the ^1H- and ^{13}C-n.m.r. data (Tables II and III; Fig. 2) was a 3:2 mixture of the monocyclic compounds **21a** and **21b**. The structures of these compounds were indicated by the n.m.r. data, namely, large paramagnetic shifts (≥1 p.p.m.) of the signals of H-1,2,3,5, the change in the $J_{2,3}$ value from 12.4 Hz in **20** to 1.8 and 1.4 Hz in **21a** and **21b**, respectively, two sets of two NAc and four OAc signals, the presence of two OMe signals (epimers at C-1), and conservation of the cyclic urea structure (151.7 p.p.m., NCON). The formation of **21a** and **21b** can be attributed to acetolysis of the strained pyranoid ring of **20** in addition to *N*- and *O*-acetylation.

Cyclic urea derivatives of saccharides have been synthesised hitherto only in special cases[11,12], and mainly in the *N*-substituted form[4,13–15]. The one-pot procedure now reported and based on the reaction of azidoamino sugars with triphenylphosphine and carbon dioxide provides a general approach to the synthesis of such compounds.

EXPERIMENTAL

General. — T.l.c. was performed on Silica Gel F_{254} (Merck) with *A*, butyl acetate–acetic acid–ethanol–water (3:2:1:1); *B*, chloroform–methanol (9:1); *C*, chloroform–methanol (95:5); and *D*, chloroform–2-propanol (95:5). Silica Gel 60 (230–400 mesh) was used for column chromatography. Optical rotations were measured with a Zeiss POLAMAT A polarimeter and i.r. spectra with a Zeiss SPECORD 75 spectrometer. N.m.r. measurements were performed with JEOL FX-100 and Bruker AM-400 spectrometers operating in the F.t. mode on solutions in $CDCl_3$ (internal Me_4Si) and D_2O (internal 1,4-dioxane); for ^{31}P measurements, external aqueous 85% H_3PO_4 was used. The ^{13}C–^1H chemical shift correlation maps were produced with the aid of a pulse sequence devised for elimination of the proton–proton couplings[16]. Microanalyses were performed in the Microanalytical Laboratory of the Institute.

N-*(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)triphenylphosphine imide* (**4**). — To a solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl azide[7] (**1**; 1.86 g, 5 mmol) in dry dichloromethane (15 mL) was added triphenylphosphine (1.40 g, 5.35 mmol) with the exclusion of water. The mixture was stored for 3 h at room temperature, dry ether (45 mL) was added, and the product was collected, washed with ether, and dried at 60° over potassium hydroxide, to give **4** (2.16 g, 71%) as colourless needles, m.p. 122–123°, $[\alpha]_D$ −15° (*c* 2.5, chloroform), R_F 0.55 (solvent *A*).

Anal. Calc. for $C_{32}H_{35}N_2O_8P$: N, 4.62; P, 5.11. Found: N, 4.60; P, 4.89.

N-*(3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-*D*-glucopyranosyl)triphenylphosphine imide* (**5**). — To a solution of 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl azide[8] (**2**; 0.33 g, 1 mmol) in dry 1,4-dioxane (2 mL) was added triphenylphosphine (0.27 g, 1.03 mmol). The mixture was stored for 1 h at room temperature

until the evolution of nitrogen ceased, and then concentrated, and the residue was treated with dry ether to give chromatographically pure **5** (0.56 g, 99%) as an amorphous solid, $[\alpha]_D$ −17° (*c* 1, chloroform), R_F 0.5 (solvent *A*).

Anal. Calc. for $C_{30}H_{33}N_2O_7P$: N, 4.96; P, 5.49. Found: N, 4.82; P, 5.68.

Reaction of 2-amino-2-deoxy-β-D-glucopyranosyl azide (**3**) *with triphenylphosphine.* — A solution of **3** (ref. 6) (0.04 g, 0.196 mmol) and triphenylphosphine (0.052 g, 0.198 mmol) in *N,N*-dimethylformamide-d_7 (0.6 mL) was stored at room temperature with the exclusion of moisture. After 1 h, the n.m.r. spectra showed that the formation of *N*-(2-amino-2-deoxy-β-D-glucopyranosyl)triphenylphosphine imide (**6**) was complete; R_F 0.3 (solvent *A*).

Addition of aqueous 70% perchloric acid (1 drop) to the mixture gave the bis(perchlorate) salt **9**. During recording of ^{13}C- and ^{31}P-n.m.r. spectra, t.l.c. detected no change, but attempts to isolate **6** and **9** were unsuccessful.

(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosylamino)triphenylphosphonium perchlorate (**7**). — A solution of **4** (0.303 g, 0.5 mmol) in aqueous 70% perchloric acid (0.2 mL) and acetic acid (2 mL) was mixed with ether (10 mL) to give crude **7** (0.33 g, 93%). Precipitation with ether from a methanolic solution afforded the salt (0.29 g, 82%), m.p. 160–164° (dec.), $[\alpha]_D$ −4° (*c* 3, chloroform), R_F 0.5 (solvent *A*); ν_{max}^{KBr} 1650 cm^{-1} (NHAc).

Anal. Calc. for $C_{32}H_{36}ClN_2O_{12}P$: Cl, 5.01; N, 3.96. Found: Cl, 4.88; N, 3.85.

N-(3,4,6-Tri-O-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl)triphenylphosphine imide bis(hydrogenperchlorate) salt (**8**). — To a solution of **5** (0.48 g, 0.85 mmol) in aqueous 70% perchloric acid (0.4 mL) and acetic acid (3 mL) was added ether (30 mL), and the precipitated crude salt was purified by repeated trituration with ether and carbon tetrachloride to give **8** (0.52 g, 80%) as an amorphous, chromatographically pure product, m.p. 130–133° (dec.), $[\alpha]_D$ +6° (*c* 3, chloroform), R_F 0.45 (solvent *A*).

Anal. Calc. for $C_{30}H_{35}Cl_2N_2O_{15}P$: Cl, 9.26; N, 3.66. Found: Cl, 8.93; N, 3.40.

Bis(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)carbodiimide (**10**). — A solution of triphenylphosphine (2.28 g, 8.7 mmol) in 1,4-dioxane (10 mL) was added to a stirred solution of **1** (2.96 g, 8 mmol) in dry 1,4-dioxane (25 mL) saturated with carbon dioxide during 40 min. Carbon dioxide was bubbled through the solution for 6 h, which was then concentrated to dryness; the residue was triturated with ethanol (25 mL) and stored at ~0° overnight. The precipitate was collected, washed with cold ethanol, and dried over potassium hydroxide to give pure **10** (2.38 g, 85%). Precipitation with light petroleum from chloroform solution gave **10** as an amorphous powder, m.p. 205–210° (dec.), $[\alpha]_D$ −27° (*c* 2, chloroform), R_F 0.5 (solvent *B*); ν_{max}^{KBr} 2150 (N=C=N), 1735 (OAc), and 1650 cm^{-1} (NHAc). N.m.r. data ($CDCl_3$): ^1H (100 MHz), δ 6.55 (d, 1 H, $J_{NH,H-2}$ 9 Hz, NH), 5.28 (t, 1 H, $J_{4,5}$ ~9 Hz, H-4), 5.07 (t, 1 H, $J_{3,4}$ ~9 Hz, H-3), 4.91 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.19 (m, 2 H, H-6,6), 3.87 (q, 1 H, $J_{2,3}$ 9 Hz, H-2), 3.80 (m, 1 H, H-5), 2.10, 2.05, 2.04, and 1.96 (4 s, each 3 H, NHAc, 3 OAc); ^{13}C (25 MHz), 170.9, 170.8, 169.4 (CO), 136.9 (N=C=N), 84.6 (C-1), 73.8 (C-3), 72.8 (C-5), 68.3 (C-4),

61.9 (C-6), 56.6 (C-2), 23.3 (NHAc-*Me*), and 20.7 p.p.m. (OAc-*Me*).

Anal. Calc. for $C_{29}H_{40}N_4O_{16}$: C, 49.71; H, 5.75; N, 8.00. Found: C, 49.70; H, 5.64; N, 7.68.

Concentration of the ethanolic mother liquor and crystallisation of the product from ethyl acetate gave triphenylphosphine oxide (1.59 g, 71%), m.p. 157°.

N,N'-*Bis(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)urea* (**11**). — To a solution of **10** (0.70 g, 1 mmol) in chloroform (7 mL) was added acetic acid (1.7 mL), and the mixture was stored at room temperature overnight. Addition of light petroleum (40 mL) then gave **11** (0.63 g, 88%), R_F 0.65 (solvent *A*). Recrystallisation from nitromethane afforded **11** as colourless prisms (0.45 g, 63%), m.p. >360°, $[\alpha]_D$ +8° (*c* 0.7, methyl sulfoxide). N.m.r. data [$(CD_3)_2SO$]: ^1H (100 MHz), δ 7.95 (d, 1 H, NH, urea), 6.95 (d, 1 H, NH, amide), 5.15–4.65 (m, 3 H, H-1,3,4), 4.30–3.60 (m, 4 H, H-2,5,6,6), 2.00, 1.96, 1.91, and 1.88 (4 s, each 3 H, NHAc, 3 OAc); ^{13}C (25 MHz), 170.1, 169.6 (Ac), 155.9 (urea), 79.6 (C-1), 73.6 (C-3), 71.9 (C-5), 68.6 (C-4), 61.9 (C-6), 51.9 (C-2), 22.8 (NHAc-*Me*), and 20.5 p.p.m. (OAc-*Me*).

Anal. Calc. for $C_{29}H_{42}N_4O_{17}$: C, 48.47; H, 5.89; N, 7.80. Found: C, 48.53; H, 6.00; N, 7.66.

*3,4,6-Tri-*O*-acetyl-1,2-(carbonyldi-imino)-1,2-dideoxy-β-*D*-glucopyranose* (**12**). — (*a*) Carbon dioxide was bubbled through a solution of **5** (1.13 g, 2 mmol) in dry 1,4-dioxane (14 mL) at room temperature for 6 h. T.l.c. (solvent *A*) then revealed no **5**, but **12** (R_F 0.7) and triphenylphosphine oxide (R_F 0.8). Concentration of the mixture and column chromatography (solvent *C*) of the residue (1.3 g) gave, first, triphenylphosphine oxide (0.52 g, 94%) and then **12** (0.51 g, 77%) which, on treatment with benzene, afforded crystalline **12** (0.40 g, 61%), m.p. 164–166°, $[\alpha]_D$ +27° (*c* 1, chloroform), R_F 0.7 (solvent *A*) and 0.4 (solvent *B*); ν_{max}^{KBr} 3340, 3240 (NH), and 1750–1690 cm^{-1} (OAc, urea CO). N.m.r. data ($CDCl_3$): ^1H (100 MHz), δ 6.30 (d, 1 H, $J_{NH,H-1}$ 3 Hz, NH), 5.99 (s, 1 H, NH), 5.21 (t, 1 H, $J_{3,4}$ ~9 Hz, H-3), 5.04 (t, 1 H, H-4), 4.78 (dd, 1 H, $J_{1,2}$ ~9 Hz, H-1), 4.25–4.1 (m, 2 H, H-6,6), 3.91 (dt, 1 H, H-5), 3.43 (t, 1 H, $J_{2,3}$ ~9 Hz, H-2), 2.10 (s, 3 H, OAc), 2.07 (s, 6 H, 2 OAc); ^{13}C (25 MHz), 170.6, 170.4, 169.7 (Ac), 162.1 (urea), 86.4 (C-1), 75.8 (C-3), 73.8 (C-5), 63.1 (C-4), 62.0 (C-6), 59.8 (C-2), and 20.6 p.p.m. (OAc-*Me*).

Anal. Calc. for $C_{13}H_{18}N_2O_8$: C, 47.27; H, 5.49; N, 8.48. Found: C, 47.31; H, 5.57; N, 8.35.

(*b*) Compound **2** (0.88 g, 2.7 mmol) was treated with triphenylphosphine (0.78 g, 3 mmol) in dry 1,4-dioxane (30 mL) in the presence of carbon dioxide as described for **10**. Concentration of the mixture and repeated trituration of the syrupy residue with benzene gave **12** (0.56 g, 64%) as colourless prisms, m.p. 163–165°.

Processing of the benzene extract gave triphenylphosphine oxide (0.57 g, 76%), m.p. 155–156°.

(*c*) Conventional treatment of **13** (0.20 g, 1 mmol) with acetic anhydride (1

mL) and pyridine (2 mL) at room temperature for 2 days, with crystallisation of the crude product (0.28 g, 85%) from benzene, gave **12** (0.19 g, 58%), m.p. 163–165°.

*1,2-(Carbonyldi-imino)-1,2-dideoxy-β-*D*-glucopyranose* (**13**). — Reaction of **3** (0.55 g, 2.7 mmol) with triphenylphosphine (0.81 g, 3.1 mmol) in dry *N,N*-dimethylformamide (20 mL) was carried out as described for **10**. After 6 h, the mixture was co-concentrated with ethanol, and the residue was triturated with chloroform to give crude **13** (0.54 g, 98%). Precipitation with ether from concentrated aqueous 96% ethanolic solution afforded **13** (0.43 g, 78%), m.p. 171–172°, $[\alpha]_D$ +37° (*c* 1.1, water), R_F 0.3 (solvent *A*): ν_{max}^{KBr} 1690 cm^{-1} (CO). ^{13}C-N.m.r. data [$(CD_3)_2SO$, 25 MHz]: δ 162.3 (CO), 86.3 (C-1), 81.5 (C-3), 75.0 (C-5), 71.8 (C-4), 62.2 (C-2), and 61.2 p.p.m. (C-6).

Anal. Calc. for $C_7H_{12}N_2O_5$: C, 41.18; H, 5.92; N, 13.72. Found: C, 41.10; H, 5.98; N, 13.27.

*3,4,6-Tri-*O*-acetyl-1,2-(di-*N*-acetylcarbonyldi-imino)-1,2-dideoxy-β-*D*-glucopyranose* (**14**). — A solution of **12** (0.29 g, 0.88 mmol) in acetic anhydride (7 mL) and trifluoroacetic acid (0.6 mL) was stored at room temperature for 1 week. T.l.c. (solvent *B*) then showed no **12** but traces of a partially acetylated compound (R_F 0.6) and **14** (R_F 0.75). The mixture was co-concentrated with ethanol, and the residue was crystallised from ethanol to give **14** (0.185 g, 51%), m.p. 175–176°, $[\alpha]_D$ −70° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H (100 MHz), δ 5.4–5.1 (m, 2 H, H-3,4), 4.94 (d, 1 H, $J_{1,2}$ ~8.5 Hz, H-1), 4.25–3.9 (m, 3 H, H-5,6,6), 3.85 (t, 1 H, $J_{2,3}$ 10 Hz, H-2), 2.52 and 2.47 (2 s, each 3 H, 2 NAc), 2.09, 2.07 and 2.06 (3 s, each 3 H, 3 OAc); ^{13}C (25 MHz), 172.2, 171.9, 171.2, 169.2 (Ac), 151.7 (urea), 83.1 (C-1), 76.6 (C-3), 72.8 (C-5), 68.4 (C-4), 61.7 (C-6), 58.9 (C-2), 25.6, 25.2 (NAc-*Me*), 20.8, 20.7, and 20.5 p.p.m. (OAc-*Me*).

Anal. Calc. for $C_{17}H_{22}N_2O_{10}$: C, 49.28; H, 5.35; N, 6.76. Found: C, 49.16; H, 5.41; N, 6.60.

*Methyl 2,3-(carbonyldi-imino)-2,3-dideoxy-α-*D*-altropyranoside* (**19**). — (*a*) To a solution of **18**·HCl[10] (0.51 g, 2 mmol) in dry methanol (10 mL) was added methanolic M sodium methoxide (2.1 mL), and the mixture was concentrated to dryness to give crude amorphous **18**. Reaction of **18** with triphenylphosphine (0.57 g, 2.18 mmol) in dry *N,N*-dimethylformamide (23 mL) in the presence of carbon dioxide was then performed as described for **10**. The mixture was co-concentrated with toluene, the residue was triturated with benzene, and the product was collected and washed with benzene, chloroform, and ether to give crude **19** (0.59 g). Precipitation with ether from concentrated ethanolic solution furnished chromatographically pure **19** (0.27 g, 62%) as an amorphous hygroscopic solid, $[\alpha]_D$ +52° (*c* 3.8, methanol), R_F 0.5 (solvent *A*); ν_{max}^{KBr} 1680 cm^{-1} (CO).

Anal. Calc. for $C_8H_{14}N_2O_5$: C, 44.03; H, 6.47; N, 12.84. Found: C, 44.17; H, 6.59; N, 12.57.

The usual work-up of the benzene fraction of trituration gave triphenylphosphine oxide (0.50 g, 90%), m.p. 154–156°.

(*b*) Conventional Zemplén deacetylation of **20** (0.30 g, 1 mmol), followed by

deionisation with Amberlite IR-120 (H^+) resin and concentration, gave amorphous **19** (0.155 g, 71%), R_F 0.5 (solvent *A*).

*Methyl 4,6-di-*O*-acetyl-2,3-(carbonyldi-imino)-2,3-dideoxy-α-*D*-altropyranoside* (**20**). — Conventional treatment of **19** (0.33 g, 1.5 mmol) with acetic anhydride (2 mL) and pyridine (3.5 mL) at room temperature for 3 days, followed by column chromatography (solvent *C*) of the product, gave **20** (0.35 g, 77%), isolated as a colourless glass, $[\alpha]_D$ +92° (*c* 1.5, chloroform), R_F 0.25 (solvent *C*); ν_{max}^{KBr} 3350, 3250 (NH), 1730 (OAc), and 1680 cm^{-1} (urea CO).

Anal. Calc. for $C_{12}H_{18}N_2O_7$: C, 47.68; H, 6.00; N, 9.27. Found: C, 47.47; H, 5.86; N, 9.14.

*1,4,5,6-Tetra-*O*-acetyl-2,3-[carbonyldi(acetylimino)]-2,3-dideoxy-1-methoxy-*D*-altritol* (**21a** *and* **21b**). — A solution of **20** (0.15 g, 0.5 mmol) in acetic anhydride (4 mL) and trifluoroacetic acid (0.3 mL) was stored at room temperature. T.l.c. (solvent *D*) showed a slow reaction; after 6 weeks, there was a preponderant product (R_F 0.55). The mixture was co-concentrated with methanol to give a syrup (0.18 g). Repeated column chromatography (solvent *D*) afforded a 3:2 mixture (0.11 g, 45%) of **21a** and **21b**, m.p. 130–132°, $[\alpha]_D$ −30° (*c* 2.8, chloroform), R_F 0.55 (solvent *D*), R_F 0.7 (solvent *C*); ν_{max}^{KBr} 1740 (OAc) and 1700–1690 cm^{-1} (NAc, urea CO).

Anal. Calc. for $C_{20}H_{28}N_2O_{12}$: C, 49.18; H, 5.78; N, 5.74. Found: C, 49.29; H, 5.85; N, 5.67.

ACKNOWLEDGMENTS

The Alexander von Humboldt-Stiftung is acknowledged for a fellowship (to G.T.), and Professor G. Snatzke for his interest.

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