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UNPROTECTED SUGAR PHOSPHINIMINES: A FACILE ROUTE TO CYCLIC CARBAMATES OF AMINO SUGARS

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ABSTRACT

Unprotected sugar phosphinimines were prepared from various azido sugars by reaction with triphenylphosphine and were converted by carbon dioxide into cyclic carbamates of amino sugars. The reaction could be carried out more conveniently in a one-pot process without isolation of the phosphinimines. The ^{13}C- and ^{31}P-n.m.r. data for *N*-(β-D-glucopyranosyl)triphenylphosphine imide (**2**) revealed an unexpected conformation of the phosphinimine moiety (proposed as a "reverse exo-anomeric effect") stabilised by an interaction with HO-2.

INTRODUCTION

Protected sugar phosphinimines[1–6] are synthons for various acyclic and cyclic nitrogen derivatives (carbodi-imides, aminotetrazoles, epimines). We describe now the first preparation of unsubstituted sugar phosphinimines which are not accessible by deblocking[5] the protected derivatives.

RESULTS AND DISCUSSION

The Staudinger reaction[7] of β-D-glucopyranosyl azide[8] (**1**) with triphenylphosphine in dry 1,4-dioxane at room temperature afforded the corresponding phosphinimines (**2**) in quantitative yield. On treatment with perchloric acid in acetic anhydride, both **2** and the authentic acetyl derivative[1,5] (**3**) furnished the same tetra-*O*-acetyl aminophosphonium salt (**4**), providing evidence for the structure of **2**. Compound **2** is stable in the crystalline form, but decomposes quickly in aqueous solution or in boiling ethanol to give β-D-glucopyranosylamine[9] and triphenylphosphine oxide. In contrast, the corresponding aminophosphonium salts **5** and **6**, obtained from **2**, were stable even in hot water.

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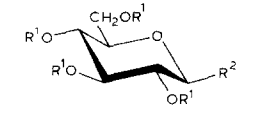
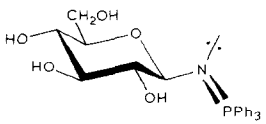


1 $R^1 = H, R^2 = N_3$
4 $R^1 = Ac, R^2 = \overset{+}{N}HPPh_3\ ClO_4^-$
5 $R^1 = H, R^2 = \overset{+}{N}HPPh_3\ ClO_4^-$
6 $R^1 = H, R^2 = \overset{+}{N}HPPh_3\ Cl^-$
23 $R^1 = H, R^2 = N{=}C{=}O$



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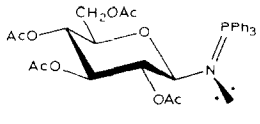

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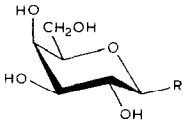
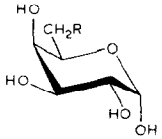
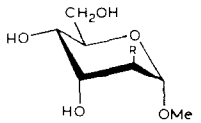


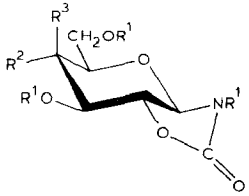
7 R = N_3
8 R = $N{=}PPh_3$
9 R = $\overset{+}{N}HPPh_3\ ClO_4^-$



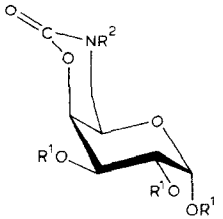
10 R = N_3
12 R = $N{=}PPh_3$



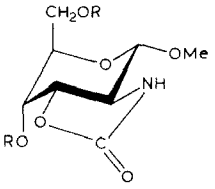
11 R = N_3
13 R = $N{=}PPh_3$



14 $R^1 = R^3 = H, R^2 = OH$
15 $R^1 = R^2 = H, R^3 = OH$
16 $R^1 = Ac, R^2 = OAc, R^3 = H$
17 $R^1 = Ac, R^2 = H, R^3 = OAc$



18 $R^1 = R^2 = H$
19 $R^1 = Ac, R^2 = H$
20 $R^1 = R^2 = Ac$



21 R = H
22 R = Ac

The phosphinimine structure of **2** was confirmed also by ^{13}C- and ^{31}P-n.m.r. data (Table I) which revealed characteristic differences between the phosphinimines (**2** and **3**) and aminophosphonium salts (**4** and **5**), particularly, in chemical shifts and ^{13}C–^{31}P couplings for C-ipso as well as in chemical shifts for the phosphorus atom, in agreement with data[10] for *N*-arylphosphinimines and their salts.

On the other hand, the signal for C-2 in **2** exhibited a surprisingly low chemical shift (67 p.p.m.), which should be higher than that (75.9 p.p.m.) in the acetylated derivative **3** since acetylation usually causes an upfield shift. In addition, a striking difference was found in the $^3J_{P,C\text{-}2}$ values for **2** (1.5 Hz) and for **3** (23.2 Hz). On the basis of the stereospecificity of $^3J_{P,C}$ couplings[11–13], the latter large value indicates the *γ-anti* orientation of P–N and C-1–C-2 bonds in **3**, *i.e.*, the lone

TABLE I

^{13}C- AND ^{31}P-N M.R DATA[a] FOR **2–5**

Compound	^{31}P *Chemical shifts*[b]	^{13}C *Chemical shifts*[c,d]					
		C-1	*C-2*	*C-ipso*	*C-ortho*	*C-meta*	*C-para*
2	20.25	91.0 (4)	67.0 (1.5)	132.1 (97.0)	133.1 (9.8)	128.6 (11.0)	131.7
3	18.89	89.2 (~1)	75.9 (23.2)	131.7 (98.3)	133.1 (9.2)	128.9 (11.2)	132.2
4	44.78	81.8 (<1.5)	71.8 (11.0)	120.0 (102.5)	134.2 (11.6)	130.3 (13.4)	135.7
5	39.18	84.7 (<1.5)	74.2 (8.5)	120.9 (103.2)	133.8 (11.0)	129.8 (13.4)	135.0

[a]Recorded at 100 MHz in $(CD_3)_2NCDO$. [b]δ Scale (external aqueous 85% H_3PO_4). [c]δ Scale (internal Me_4Si). [d]Couplings (Hz) of ^{31}P with the corresponding ^{13}C in parentheses.

pair of the nitrogen atom is oriented antiperiplanar to the C–O bond of the pyranoid ring. This conformer allows a stabilising electron interaction (n $\rightarrow$ σ^*) required by the exo-anomeric effect[14].

In contrast, the small value of $^3J_{P,C}$ in **2** reflects a conformation in which the orientation of the P–N bond is *γ-gauche* related to the C-1–C-2 bond, *i.e.*, anti-periplanar to the C–O bond of the pyranoid ring. This conformer can be stabilised by an interaction between the phosphinimine bond and HO-2 (either P $\rightarrow$ O or hydrogen bond interaction). The latter conformation (**2**), being opposite to that (**3**) stabilised by the exo-anomeric effect, might be considered as a special case of the "reverse exo-anomeric effect".

The reaction of β-D-galactopyranosyl azide[8] (**7**) with triphenylphosphine also afforded a stable phosphinimine (**8**), which was treated with perchloric acid to give the corresponding salt (**9**). On the other hand, although the reaction of 6-azido-6-deoxy-α-D-galactose[5] (**10**) and methyl 2-azido-2-deoxy-α-D-altroside[15] (**11**) with triphenylphosphine gave (t.l.c.) the corresponding phosphinimines (**12** and **13**), they were not sufficiently stable to be isolated.

Whereas protected sugar phosphinimines react with carbon dioxide to produce carbodi-imides[1], the reaction of the unsubstituted glucosyl (**2**) and galactosyl (**8**) phosphinimines with carbon dioxide in *N,N*-dimethylformamide gave cyclic carbamates **14** and **15**, respectively. The structures of the cyclic carbamates and their acetyl derivatives **16** and **17** were established on the basis of i.r., ^1H- and ^{13}C-n.m.r. data. Diequatorial *trans*-annelation of the oxazolidine and pyranoid rings was proved by the large $J_{1,2}$ values (9.2 Hz) for **16** and **17**. Consequently, *cis*-annelation of the rings, suggested earlier[16] for **14** and **16**, is incorrect.

The cyclic carbamates are also accessible by a one-pot method based on preparation of the phosphinimines *in situ*. In the presence of carbon dioxide in acetone, **1** and **7** were treated with triphenylphosphine to give the carbamates **14**

and **15**, respectively. Using this procedure, the non-glycosidic azides **10** and **11** could be converted into the crystalline cyclic carbamates **18** and **21**, respectively. Conventional treatment of **18** with acetic anhydride–pyridine effected only *O*-acetylation, affording **19**, as was shown by three singlets for *O*-acetyl groups (δ 2.16, 2.09, and 2.0) in the ^{1}H-n.m.r. spectrum. *N*-Acetylation of **19** to give **20** required heating with sodium acetate–acetic anhydride. Accordingly, the ^{1}H-n.m.r. spectrum of **20** contained an additional singlet for *N*-acetyl (δ 2.59). That both **19** and **20** are α anomers was established by $J_{1,2}$ values (3.3 and 3.2 Hz, respectively). For the 2,3-(cyclic carbamate) **21** and its 4,6-diacetate **22**, the $^1C_4$ conformation of the pyranoid ring required for the fused five-membered oxazolidine ring was supported by the large values of $J_{1,2}$ and $J_{2,3}$ in the spectra of **21** and **22**.

The formation of the cyclic carbamates can be attributed to the intramolecular cyclisation of the isocyanate intermediates (*e.g.*, **23**), formed from the phosphinimines with carbon dioxide, with participation of a sterically favoured OH group.

Intramolecular carbamates of amino sugars and aminocyclitols have recently attracted interest since they enable simultaneous protection of amino and hydroxyl groups[17–21]. The conversion of azido sugars into cyclic carbamates by reaction with triphenylphosphine–carbon dioxide is a novel and simple route to 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*, carbon tetrachloride–ethyl acetate (3:2); and *C*, carbon tetrachloride–ethyl acetate–ethanol (3:2:1). Optical rotations were measured with a Zeiss POLAMAT A polarimeter. I.r. spectra were recorded with a Zeiss Infracord 75 spectrometer. The ^{1}H-, ^{13}C-, and ^{31}P-n.m.r. spectra were recorded with a JEOL FX-100 instrument. Microanalyses were performed in the Microanalytical Laboratory of the Institute.

N-*(β-D-Glucopyranosyl)triphenylphosphine imide* (**2**). — To a solution of β-D-glucopyranosyl azide[8] (**1**; 2.05 g, 10 mmol) in dry 1,4-dioxane (25 mL) was added a solution of triphenylphosphine (2.95 g, 11.25 mmol) in dry 1,4-dioxane (10 mL) at room temperature. The evolution of nitrogen ceased and separation of the crystals of **2** began within 15 min. After storage of the mixture for 2 h at room temperature, the product was collected, washed with dry 1,4-dioxane and ether, and dried over potassium hydroxide in a desiccator to give chromatographically pure **2** (4.35 g, 99%), m.p. 118–120°, $[\alpha]_D$ −6° (*c* 2, acetic acid), R_F 0.4 (solvent *A*).

Anal. Calc. for $C_{24}H_{26}NO_5P$: N, 3.19; P, 7.05. Found: N, 2.90; P, 6.94.

Hydrolysis of **2**. — (*a*) A solution of **2** (0.44 g, 1 mmol) in water (4.5 mL) was stored at room temperature for 4 h and then at ~0° overnight; separation of triphenylphosphine oxide started within 5 min. The crystals were collected and washed with water to give triphenylphosphine oxide (0.24 g, 86%), m.p. 155–157°, R_F 0.8 (solvent *A*). Concentration of the filtrate afforded β-D-glucopyranosylamine[9] (0.17 g, 95%), m.p. 127–128°, $[\alpha]_D$ +22.5° (*c* 1, water).

(*b*) A solution of **2** (0.44 g, 1 mmol) in dry ethanol (5 mL) was boiled for 5 min, and then stored at ~0° to give β-D-glucopyranosylamine (0.13 g, 73%), m.p. 128–129°, $[\alpha]_D$ +23° (*c* 1, water). Concentration of the mother liquor and crystallisation of the residue from ethyl acetate yielded triphenylphosphine oxide (0.22 g, 79%), m.p. 153–155°.

Triphenyl(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylamino)phosphonium perchlorate (**4**). — (*a*) To a mixture of aqueous 70% perchloric acid (0.4 mL) and acetic anhydride (5 mL) was added **2** (0.44 g, 1 mmol) at 0°, and the mixture was stirred at room temperature for 1 h. Addition of ether (60 mL) gave crude **4** (0.60 g, 85%), which was recrystallised from water to afford the pure salt (0.40 g, 56%), m.p. 207–208° (dec.), $[\alpha]_D$ +3.5° (*c* 2, chloroform).

Anal. Calc. for $C_{32}H_{35}ClNO_{13}P$: Cl, 5.01; N, 1.98. Found: Cl, 4.88; N, 2.08.

(*b*) To an ice-cold mixture of aqueous 70% perchloric acid (0.4 mL) and acetic anhydride (5 mL) was added *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-triphenylphosphine imide[5] (**3**; 0.61 g, 1 mmol), and the crude salt (0.70 g, 99%) was precipitated with ether (60 mL). Recrystallisation from water gave **4** (0.49 g, 69%), m.p. 207–208° (dec.), $[\alpha]_D$ +4° (*c* 2, chloroform), identical with the product in (*a*).

(β-D-Glucopyranosylamino)triphenylphosphonium perchlorate (**5**). — A solution of **2** (0.22 g, 0.5 mmol) in aqueous 70% perchloric acid (0.2 mL) and ethanol (2 mL) was mixed with ether (20 mL) to give crude **5** (0.25 g, 93%), m.p. 166–169°. Precipitation with ether from methanolic solution afforded the pure salt (0.20 g, 74%), m.p. 173–174°, $[\alpha]_D$ +7° (*c* 2, methanol).

Anal. Calc. for $C_{24}H_{27}ClNO_9P$: Cl, 6.57; N, 2.59. Found: Cl, 6.37; N, 2.69.

(β-D-Glucopyranosylamino)triphenylphosphonium chloride (**6**). — To a solution of **2** (0.22 g, 0.5 mmol) in methanolic 5% hydrogen chloride (5 mL) was added ether (50 mL) to give **6** (0.20 g, 84%), m.p. 188–191° (dec.). Addition of ether to a methanolic solution precipitated the pure salt (0.16 g, 67%), m.p. 188–190° (dec.), $[\alpha]_D$ +8° (*c* 2, methanol), R_F 0.4 (solvent *A*).

Anal. Calc. for $C_{24}H_{27}ClNO_5P$: Cl, 7.45; N, 2.94. Found: Cl, 7.45; N, 2.86.

N-(β-D-Galactopyranosyl)triphenylphosphine imide (**8**). — To a solution of β-D-galactopyranosyl azide[8] (**7**; 0.82 g, 4 mmol) in dry 1,4-dioxane (18 mL) was added triphenylphosphine (1.15 g, 4.4 mmol), and the solution was stored at room temperature for 3 h with exclusion of water. Addition of dry ether then gave **8** (1.20 g, 68%) as an amorphous powder, $[\alpha]_D$ +3° (*c* 2, acetic acid), R_F 0.4 (solvent *A*).

Anal. Calc. for $C_{24}H_{26}NO_5P$: N, 3.19; P, 7.05. Found: N, 3.44; P, 7.01.

(β-D-Galactopyranosylamino)triphenylphosphonium perchlorate (**9**). — Compound **8** (0.44 g, 1 mmol) was treated with ethanolic perchloric acid and processed, as described for the preparation of **5**, to yield **9** (0.30 g, 55%) as an amorphous powder (from methanol–ether), $[\alpha]_D$ +10° (*c* 1, methanol).

Anal. Calc. for $C_{24}H_{27}ClNO_9P$: Cl, 6.57; N, 2.59. Found: Cl, 6.49; N, 2.36.

β-D-Glucopyranosylamine 1,2-(cyclic carbamate) (**14**). — (*a*) Compound **2** (0.90 g, 2 mmol) was dissolved in dry *N,N*-dimethylformamide (10 mL), previously saturated with carbon dioxide, at room temperature and the flow of carbon dioxide

was continued for 1 h. T.l.c. (solvent *A*) then revealed no **2** and the formation of **14** (R_F 0.45) and triphenylphosphine oxide (R_F 0.8). The solution was repeatedly co-concentrated with toluene, and the residue was triturated with chloroform (10 mL) to give **14** (0.34 g, 81%), m.p. 224°. Recrystallisation from methanol–water (9:1) furnished **14** (0.23 g, 55%) as colourless prisms, m.p. 224–226°, $[\alpha]_D$ +56° (*c* 2, water); ν_{max}^{KBr} 3450–3200 (OH, NH), and 1745 cm^{-1} (CO); lit.[16] m.p. 220–222°, $[\alpha]_D$ +56° (water). N.m.r. data (D_2O): ^1H, δ 4.96 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1); ^{13}C, 160.9 (CO), 85.9 (C-1), 82.5, 81.4 (C-5, C-3), 73.6 (C-2), 72.0 (C-4), and 61.3 p.p.m. (C-6).

Anal. Calc. for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 41.18; H, 5.63; N, 6.90.

Concentration of the chloroform filtrate and crystallisation of the residue gave triphenylphosphine oxide (0.45 g, 79%), m.p. 155°.

(*b*) To a solution of **1** (1.44 g, 7 mmol) in dry acetone (40 mL) saturated with carbon dioxide was added a solution of triphenylphosphine (1.92 g, 7.3 mmol) in acetone (20 mL) at room temperature during 20 min. Carbon dioxide was bubbled through the solution for 5 h, and the mixture was then stored overnight. The precipitate was collected, and washed with acetone and ether to give **14** (1.31 g, 91%), m.p. 224–226°, identical with the product in (*a*).

Processing of the mother liquor afforded triphenylphosphine oxide (1.58 g, 81%), m.p. 154–156°.

N-*Acetyl-3,4,6-tri*-O-*acetyl*-β-D-*glucopyranosylamine 1,2-(cyclic carbamate)* (**16**). — Conventional treatment of **14** (0.50 g, 2.44 mmol) with acetic anhydride (2.5 mL) and pyridine (4 mL) at room temperature for 24 h and crystallisation of the product (0.51 g, 56%) from ethanol gave **16** as colourless needles (0.44 g, 48%), m.p. 150–151°, $[\alpha]_D$ +21° (*c* 2, chloroform), R_F 0.25 (solvent *B*) and 0.75 (solvent *C*); lit.[16] m.p. 150–151°, $[\alpha]_D$ +12.14° (chloroform); ν_{max}^{KBr} 1820 (carbamate CO), 1755–1745 (OAc), and 1720 cm^{-1} (NAc). N.m.r. data ($CDCl_3$): ^1H, δ 5.44 (dd, 1 H, $J_{3,4}$ 8.2 Hz, H-3), 5.14 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.13 (d, 1 H, $J_{1,2}$ 9.2 Hz, H-1), 4.30–4.15 (m, 3 H, H-5,6,6), 4.02 (dd, 1 H, $J_{2,3}$ 10.6 Hz, H-2), 2.52 (s, 3 H, NAc), 2.10 (s, 6 H, 2 OAc), 2.08 (s, 3 H, OAc); ^{13}C, 171.0, 170.4, 169.8, 169.4 (CO), 84.4 (C-1), 76.7 (C-5), 76.1 (C-3), 71.1 (C-2), 68.3 (C-4), 61.4 (C-6), 24.3 (NAc-Me), and 20.6 p.p.m. (OAc-Me).

Anal. Calc. for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.19; H, 5.71; N, 3.87.

β-D-Galactopyranosylamine 1,2-(cyclic carbamate) (**15**). — (*a*) A solution of **8** (0.60 g, 1.37 mmol) in dry *N,N*-dimethylformamide (10 mL) at room temperature was treated with carbon dioxide for 4 h and processed as described for **14** [method (*a*)] to give **15** (0.25 g, 89%), m.p. 196°, R_F 0.45 (solvent *A*). Recrystallisation from nitromethane gave colourless needles, m.p. 197–199°, $[\alpha]_D$ +84° (*c* 1, water); ν_{max}^{KBr} 3500–3250 (OH, NH) and 1755 cm^{-1} (CO). ^{13}C-N.m.r. data (D_2O): δ 160.7 (CO), 86.8 (C-1), 81.7 (C-3), 80.9 (C-5), 70.6, 70.4 (C-2,4), and 61.6 p.p.m. (C-6).

Anal. Calc. for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.96; H, 5.77; N, 6.77.

(*b*) Reaction of **7** (3.07 g, 15 mmol) with triphenylphosphine (4.13 g, 15.75 mmol) in the presence of carbon dioxide was carried out as described for **14** [method (*b*)]. After 24 h, the reaction mixture was concentrated and the residue was triturated with chloroform (30 mL) to give almost pure **15** (2.92 g, 95%), R_F 0.45 (solvent *A*). Recrystallisation from nitromethane furnished **15** as long needles, m.p. 197–199°, identical with the product in (*a*). Concentration of the chloroform filtrate gave triphenylphosphine oxide (3.99 g, 96%).

N-*Acetyl-3,4,6-tri*-O-*acetyl*-β-D-*galactopyranosylamine 1,2-(cyclic carbamate)* (**17**). — Conventional treatment of **15** (0.20 g, 1 mmol) with acetic anhydride (1 mL) and pyridine (1.7 mL) at room temperature for 4 days, with crystallisation of the crude product (0.22 g, 60%) from ethanol, gave **17** as colourless crystals (0.16 g, 44%), m.p. 191–193°, $[\alpha]_D$ +14° (*c* 1, chloroform), R_F 0.25 (solvent *B*) and 0.75 (solvent *C*); ν_{max}^{KBr} 1800 (carbamate CO), 1750 (OAc), and 1720 cm^{-1} (NAc). N.m.r. data ($CDCl_3$): ^1H, δ 5.52 (dd, 1 H, $J_{4,5}$ 1.1 Hz, H-4), 5.33 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3), 5.04 (d, 1 H, $J_{1,2}$ 9.2 Hz, H-1), 4.38 (dd, 1 H, $J_{2,3}$ 11.3 Hz, H-2), 4.30–4.05 (m, 3 H, H-5,6,6), 2.51 (s, 3 H, NAc), 2.13 (s, 3 H, OAc), 2.03 (s, 6 H, 2 OAc); ^{13}C, 170.7, 169.9, 169.3, 169.2 (CO), 85.5 (C-1), 75.4 (C-5), 74.4 (C-3), 69.0 (C-2), 67.1 (C-4), 60.3 (C-6), 23.8 (NAc-Me), 20.2, 20.0, and 20.0 p.p.m. (OAc-Me).

Anal. Calc. for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.37; H, 5.34; N, 3.71.

6-Amino-6-deoxy-α-D-*galactopyranose 6,4-(cyclic carbamate)* (**18**). — To a solution of 6-azido-6-deoxy-α-D-galactopyranose[5] (**10**; 2.88 g, 14 mmol) in dry *N,N*-dimethylformamide (36 mL) saturated with carbon dioxide was added a solution of triphenylphosphine (3.90 g, 14.9 mmol) in *N,N*-dimethylformamide (40 mL) during 3 h. Carbon dioxide was bubbled through the mixture for 8 h which was then stored overnight. The mixture was cooled, and the crystals were collected and washed with chloroform to yield **18** (1.73 g, 60%), m.p. 205–206° (dec.), R_F 0.2 (solvent *A*). Concentration of the mother liquor and trituration of the residue with chloroform gave more **18** (0.93 g). Precipitation with acetone from aqueous solution furnished colourless prisms of **18** (2.15 g, 75%), m.p. 206–208° (dec.), $[\alpha]_D$ +212→ +162° (*c* 1.9, water); ν_{max}^{KBr} 3400–3200 (OH, NH) and 1670 cm^{-1} (CO).

Anal. Calc. for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.89; H, 5.55; N, 6.84.

Usual work-up of the chloroform mother-liquor afforded triphenylphosphine oxide (2.76 g, 71%), m.p. 155–156°.

1,2,3-Tri-O-*acetyl-6-amino-6-deoxy*-α-D-*galactopyranose 6,4-(cyclic carbamate)* (**19**). — Conventional treatment of **18** (0.70 g, 3.4 mmol) with acetic anhydride (3.5 mL) and pyridine (6.2 mL) at room temperature for 3 days gave crude **19** (0.92 g, 81%), R_F 0.6 (solvent *A*). Recrystallisation from methanol afforded **19** (0.83 g, 73%) as colourless plates, m.p. 244–246° (dec.), $[\alpha]_D$ +259° (*c* 0.4, nitromethane); ν_{max}^{KBr} 3330 (NH), 1745, 1720 (OAc), and 1680 cm^{-1} (CO, carbamate). ^1H-N.m.r. [$(CD_3)_2SO$]: δ 7.37 (d, 1 H, NH), 6.18 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 5.31 (dd, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 5.12 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2), 4.82 (dd, 1 H, $J_{4,5}$ <1

Hz, H-4), 4.43 (m, 1 H, $J_{5,6a}$ 3.5, $J_{5,6e}$ <1 Hz, H-5), 3.46 (dd, 1 H, $J_{6a,6e}$ 13.8 Hz, H-6*a*), 3.10 (ddd, 1 H, H-6*e*), 2.16, 2.09, and 2.0 p.p.m. (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{13}H_{17}NO_9$: C, 47.13; H, 5.17; N, 4.23. Found: C, 47.11; H, 5.33; N, 4.37.

N-*Acetyl-1,2,3-tri*-O-*acetyl-6-amino-6-deoxy-α*-D-*galactopyranose 6,4-(cyclic carbamate)* (**20**). — A mixture of **19** (0.25 g, 0.75 mmol), dry sodium acetate (0.20 g), and acetic anhydride (1.5 mL) was boiled under reflux for 1 h, then poured into ice–water, and extracted with chloroform, and the extract was washed with aqueous sodium hydrogencarbonate and water, dried, and concentrated to give **20** (0.24 g, 86%) as a chromatographically homogeneous syrup, R_F 0.75 (solvent *A*). Precipitation with light petroleum from chloroform solution yielded **20** (0.18 g, 63%) as an amorphous solid, $[\alpha]_D$ +239° (*c* 1.2, chloroform); ν_{max}^{KBr} 1760–1730 (OAc, carbamate CO) and 1700 cm^{-1} (NAc). ^{1}H-N.m.r. data ($CDCl_3$): δ 6.38 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.44 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2), 5.30 (dd, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 4.87 (dd, 1 H, $J_{4,5}$ 0.7 Hz, H-4), 4.53 (m, 1 H, H-5), 4.15 (dd, 1 H, $J_{5,6e}$ 1.7, $J_{6a,6e}$ 14.7 Hz, H-6*e*), 3.60 (dd, 1 H, $J_{5,6a}$ 3.6 Hz, H-6*a*), 2.59 (s, 3 H, NAc), 2.18, 2.16, and 2.03 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.49; H, 5.39; N, 3.87.

Methyl 2-amino-2-deoxy-α-D-*altropyranoside 2,3-(cyclic carbamate)* (**21**). — A solution of methyl 2-azido-2-deoxy-α-D-altropyranoside[15] (**11**; 0.88 g, 4 mmol) in dry acetone was treated with triphenylphosphine (1.16 g, 4.4 mmol) in the presence of carbon dioxide at room temperature. After 6 h, t.l.c. (solvent *A*) revealed **21** (R_F 0.5) and triphenylphosphine oxide (R_F 0.8) as the main products. Concentration of the mixture and treatment of the residue with chloroform (20 mL) gave crude **21** (0.80 g, 91%), m.p. 137–139°. Crystallisation from acetonitrile afforded **21** (0.54 g, 61%) as colourless cubes, m.p. 138–140° (dec.), $[\alpha]_D$ +75° (*c* 1, water); ν_{max}^{KBr} 3440–3200 (OH, NH) and 1730–1715 cm^{-1} (carbamate CO). ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 7.97 (s, 1 H, NH), 5.46 (d, 1 H, $J_{4,OH}$ 4.5 Hz, HO-4), 4.84 (t, 1 H, $J_{6,OH}$ 5 Hz, HO-6), 4.78 (d, 1 H, $J_{1,2}$ 6.5 Hz, H-1), 4.15–3.9 (m, 2 H, H-3,4), 3.68 (dd, 1 H, $J_{2,3}$ ~12 Hz, H-2), 3.62–3.30 (m, 3 H, H-5,6,6), and 3.33 (s, 3 H, OMe).

Anal. Calc. for $C_8H_{13}NO_6$: C, 43.84; H, 5.98; N, 6.39. Found: C, 44.12; H, 5.99; N, 6.39.

From the chloroform filtrate, triphenylphosphine oxide (0.91 g, 82%), m.p. 153–154°, was obtained.

Methyl 4,6-di-O-*acetyl-2-amino-2-deoxy-α*-D-*altropyranoside 2,3-(cyclic carbamate)* (**22**). — Conventional treatment of **21** (0.35 g, 1.6 mmol) with acetic anhydride (1.5 mL) and pyridine (2.5 mL) for 24 h, with recrystallisation of the crude product from ethanol, gave **22** (0.31 g, 64%), m.p. 168–170°, $[\alpha]_D$ +68° (*c* 1.9, chloroform), R_F 0.55 (solvent *C*); ν_{max}^{KBr} 3255 (NH), 1780 (carbamate CO), and 1745–1720 cm^{-1} (OAc). ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 8.22 (s, 1 H, NH), 5.32 (dd, 1 H, H-4), 4.82 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.34 (dd, 1 H, $J_{3,4}$ 5 Hz, H-3), 4.3–3.9 (m, 3 H, H-5,6,6), 3.67 (dd, 1 H, $J_{2,3}$ 12.5 Hz, H-2), 3.32 (s, 3 H, OMe), 2.08 and 2.02 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{12}H_{17}NO_8$: C, 47.53; H, 5.65; N, 4.62. Found: C, 47.25; H, 5.97; N, 4.60.

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