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Note

Synthesis of sugar ureas via phosphinimines

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In the course of our studies on the reactivity of sugar phosphinimines, we have found that, in the presence of carbon dioxide, phosphinimines behave like masked sugar isocyanates [1].

We now report an application of the reaction for the synthesis of substituted sugar urea derivatives. Sugar phosphinimines **1–5** were prepared in situ from azidosugars **6–10** and subsequently converted by treatment with amines and carbon dioxide into the corresponding urea derivatives (**11–15**).

In a typical experiment, a solution of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**6a**) [2] and *N*-methylpiperazine in dry tetrahydrofuran was saturated with dry carbon dioxide at ambient temperature, then treated with triphenylphosphine. After a few hours, 2,3,4,6-tetra-*O*-acetyl-*N*-(4-methylpiperazinocarbonyl)-β-D-glucopyranosylamine (**11a**) was obtained in 85% yield (Table 1) after chromatographic separation from triphenylphosphine oxide simultaneously formed in the reaction.

When **6a** was treated under similar conditions but with various secondary amines, such as morpholine, piperidine, pyrrolidine and diisopropylamine, the expected urea compounds (**11c–f**) were isolated in high yields (Table 1).

During the reactions, no deacetylation was observed due to the formation of alkylammonium salts of *N*-alkylcarbamic acids (e.g. **16**) from secondary amines and carbon dioxide [3], which neutralized the strongly basic amines.

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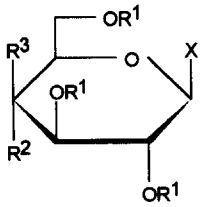
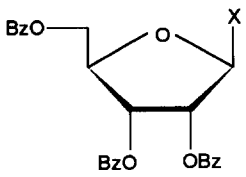
Table 1
Substituted sugar urea derivatives from azido sugars

Compound	Yield (%)	mp (°C)	$[\alpha]_D$	(solvent, *c*)	ν_{max}
11a	85	180–182	−13.0°	($CHCl_3$, 2)	3421 (NH), 1751, 1733 (AcO), 1666 (NCON)
11b	98 [a]	134–136	−21.5°	(H_2O, 2)	3402–3377 (OH, NH), 1636 (NCON)
11c	86	amorphous	−9.1°	($CHCl_3$, 2)	3402 (NH), 1751 (AcO), 1663 (NCON)
11d	94	113–114	−11.9°	($CHCl_3$, 2)	3422 (NH), 1751, 1734 (AcO), 1664 (NCON)
11e	92	179–180	−11.9°	(MeOH, 5)	3388 (NH), 1748, 1733 (AcO), 1669 (NCON)
11f	89	156–157	−12.7°	(MeOH, 5)	3464 (NH), 1751 (AcO), 1665 (NCON)
11g	75	96–98 [b]	+ 3.0°	($CHCl_3$, 3) [b]	3459, 3367 (NH), 1756, 1752 (AcO), 1667 (NCON)
12a	74	amorphous	−13.7°	(MeOH, 3)	3406 (NH), 1751, 1750 (AcO), 1658 (NCON)
12b	95	110–113	+14.1°	(AcOH, 5)	3403–3365 (OH, NH), 1637 (NCON)
13	98	amorphous	−48.4°	($CHCl_3$, 3)	3414 (NH), 1727 (BzO), 1637 (NCON)
14	65	89–91	+67.5°	($CHCl_3$, 3)	3427 (NH), 1642 (NCON)
15	88	amorphous	−38.9°	($CHCl_3$, 3)	3409 (NH), 1637 (NCON)

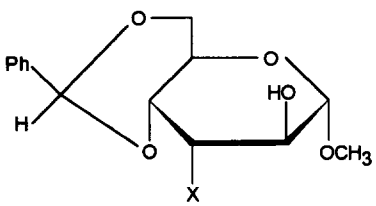
[a] Yield 88% from **17**. [b] Lit[4] mp 97–98°C; $[\alpha]_D$ +3.7° ($CHCl_3$, *c* 6).



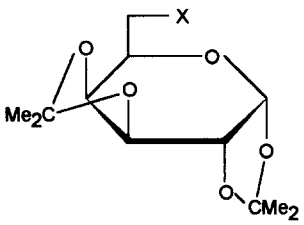
	R^1	R^2	R^3	X
1a	Ac	OAc	H	$N{=}PPh_3$
1b	H	OH	H	$N{=}PPh_3$
2a	Ac	H	OAc	$N{=}PPh_3$
2b	H	H	OH	$N{=}PPh_3$
6a	Ac	OAc	H	N_3
6b	H	OH	H	N_3
7a	Ac	H	OAc	N_3
7b	H	H	OH	N_3



3 X: $N{=}PPh_3$
8 X: N_3



4 X: $N{=}PPh_3$
9 X: N_3

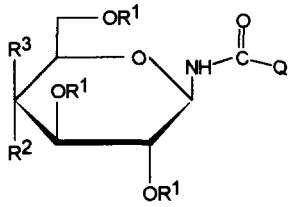


5 X: $N{=}PPh_3$
10 X: N_3

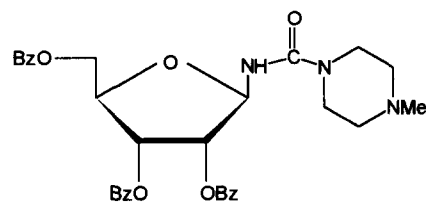
In accordance, under the same conditions, azide **6a** with ammonia easily afforded 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylurea (**11g**) (Table 1) synthesised earlier with difficulties [4].

Extension of the reaction to various protected azido sugars, such as **7a** [5], **8** [6], **9** [7] and **10** [8], with triphenylphosphine, carbon dioxide and *N*-methylpiperazine resulted in the synthesis of the corresponding protected *N*-(4-methylpiperazinocarbonyl)amino sugars (**12a, 13–15**) in excellent yields (Table 1).

Zemplén deacetylation of **11a** gave **11b**, which was otherwise obtained as sole product from the reaction of the cyclic carbamate **17** [1b] with *N*-methylpiperazine. On the other hand, β-D-galactopyranosyl azide (**7b**) [9] with triphenylphosphine, carbon dioxide, and *N*-methylpiperazine afforded the analogous unprotected galactosylurea derivative **12b** in almost quantitative yield.



	R^1	R^2	R^3	Q
11a	Ac	OAc	H	
11b	H	OH	H	
11c	Ac	OAc	H	
11d	Ac	OAc	H	
11e	Ac	OAc	H	
11f	Ac	OAc	H	iPr_2N
11g	Ac	OAc	H	NH_2
12a	Ac	H	OAc	
12b	H	H	OH	



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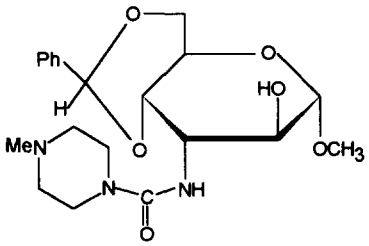

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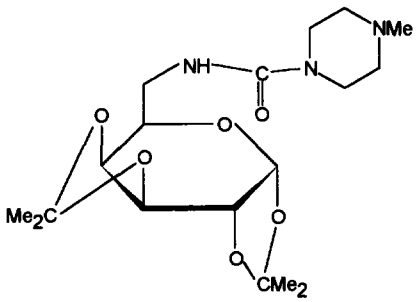

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Comparison of these results suggests that the formation of glycosylurea compounds from free glycosyl azides might proceed through either glycosylphosphinimine or 1,2-cyclic carbamate intermediates.

Evidence for the structures of the new products was obtained from their IR spectra (Table 1). Bands for NH were found between 3464 and 3367 cm^{-1} and those for the NCON group appeared between 1669 and 1636 cm^{-1}, beside the characteristic frequencies of the ester carbonyls (1756–1727 cm^{-1}) in the case of the acylated glycosyl compounds.

The proposed structures were corroborated by ^1H and ^{13}C NMR spectra of the products (Tables 2 and 3). The protons and carbon atoms of the carbohydrate moieties were unambiguously assigned as well as the H-2′-6′ and C-2′-6′ atoms of the secondary amine subunits. The carbonyl carbon atom of the urea group exhibited signals in the

Table 2
^{1}H NMR data for the substituted sugar urea derivatives

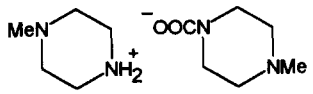
Compound	Chemical shifts (δ)								
	H-1	H-2	H-3	H-4	H-5	H-6a [a]	H-6b	NH	Others
11a [b]	5.17	4.92	5.33	5.07	3.84	4.35	4.08	5.62	3.36(H-2′,6′), 2.37(H-3′,5′), 2.30(NMe), 2.08(3H), 2.06(3H), 2.03(6H)(AcO)
11b [c]	4.61		———3.0–3.2 [d]———			3.62	3.38	6.90	3.29(H-2′,6′), 2.25(H-3′,5′), 2.18(NMe),
11c [b]	5.19	4.93	5.34	5.07	3.86	4.35	4.08	5.77	3.66(H-3′,5′), 3.34(H-2′,6′), 2.08(3H), 2.03(6H)(AcO)
11d [b]	5.20	4.93	5.33	5.07	3.86	4.36	4.08	5.61	3.30(H-2′,6′), 1.55(H-3′,4′,5′), 2.08(3H), 2.05(3H), 2.02(6H)(AcO)
11e [b]	5.20	4.94	5.33	5.07	3.85	4.33	4.08	5.35	3.33(H-2′,5′), 1.89(H-3′,4′), 2.08(3H), 2.06(3H), 2.03(6H)(AcO)
11f [b]	5.23	4.96	5.32	5.08	3.81	4.36	4.08	5.23	3.72(NCH), 2.08(3H), 2.04(3H), 2.03(3H), 2.02(3H)(AcO), 1.24(CMe)
12a [b]	———5.05–5.20 [d]———			5.44		———4.05–4.20 [d]———		5.66	3.40(H-2′,6′), 2.43(H-3′,5′), 2.31(NMe), 2.14, 2.07, 2.04, 2.00(3H each)(AcO)
12b [e]	4.60	—3.30–3.55 [d]—		3.68		———3.30–3.55 [d]———		6.89	3.32(H-2′,6′), 2.25(H-3′,5′), 2.17(NMe),
13 [f]	6.01	5.62	5.81	4.49	4.68			5.82	8.07, 7.99, 7.92(2H each), 7.6-7.3(9H) (Ph), 4.56(H-5b), 3.38(H-2′,6′), 2.34 (H-3′,5′) 2.25(NMe)
14 [b]	4.68	3.93	4.75	4.15	3.85	4.23	3.76	5.67	7.3(Ph), 5.37(OH), 5.35(CH), 3.42(MeO), 3.35(H-2′,6′), 2.39(H-3′,5′), 2.26(NMe)
15 [b]	5.51	4.30	4.59	4.23	3.92	3.67	3.21	5.02	3.38(H-2′,6′), 2.29(NMe), 2.28(H-3′,5′), 1.49, 1.44, 1.34, 1.32(3H each)(CMe)
	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{H\text{-}1,NH}$	Others
11a	9.6	9.6	9.5	9.5	3.9	2.2	12.7	8.8	
11b	8.5				2.0	5.7	11.7	8.5	
11c	9.3	9.3	9.3	9.9	3.9	2.0	12.5	9.3	
11d	9.5	9.5	9.5	9.5	3.9	2.0	12.5	9.0	
11e	9.3	9.6	9.3	9.9	4.1	2.0	12.4	9.3	
11f	9.3	9.3	9.3	9.5	3.9	2.0	12.4		
12a			2.9	0				8.8	
12b			3.0	0				8.8	
13	6.8	5.8	3.3	3.2				8.7	$J_{4,5b}$ = 4.4 Hz, $J_{5a,5b}$ = 11.2 Hz
14	0	2.7	4.1	9.5	4.1	9.5	9.5		$J_{H\text{-}3,NH}$ = 9.0 Hz
15	4.9	2.3	8.1	2.0	3.4	8.8	14.2		$J_{H\text{-}6a,NH}$ = 7.8 Hz, $J_{H\text{-}6b,NH}$ = 3.3 Hz

[a] The signal of higher chemical shift of CH_2-6 is assigned to H-6a. [b] Recorded at 250 MHz in $CDCl_3$. [c] Recorded at 400 MHz in $(CD_3)_2SO$. [d] Strongly overlapped signals. [e] Recorded at 250 MHz in $(CD_3)_2SO$. [f] Recorded at 400 MHz in $CDCl_3$.

Table 3
^{13}C NMR data [a] for the substituted sugar urea derivatives

Compound	Chemical shifts (δ)							
	C-1	C-2	C-3	C-4	C-5	C-6	NCON	Others
11a [b]	80.6	70.8	72.6	68.2	73.0	61.6	155.3	171.5, 170.6, 169.8, 169.5(COO), 54.4(C-3′,5′), 46.0 (NCH_3), 43.4(C-2′,6′), 20.7, 20.6, 20.5(2×)(CH_3COO)
11b [c]	82.0	72.1	77.7	70.1	78.2	61.0	156.5	54.5(C-3′,5′), 45.7(NCH_3), 43.1(C-2′,6′)
11c [b]	80.4	70.7	72.6	68.1	73.0	61.5	155.6	171.4, 170.5, 169.7, 169.5(COO), 66.2(C-3′,5′), 43.7(C-2′,6′), 20.6(2×), 20.4(2×)(CH_3COO)
11d [b]	80.7	70.7	72.7	68.2	73.0	61.6	155.3	171.9, 170.4, 169.7, 169.4(COO), 44.6(C-2′,6′), 25.4(C-3′,5′), 24.1(C-4′), 20.6(2×),20.4(2×)(CH_3COO)
11e [b]	80.2	70.7	72.7	68.3	72.9	61.7	154.5	171.3, 170.5, 169.7, 169.5(COO), 45.4(C-2′,6′), 25.3(C-3′,5′), 20.7, 20.6, 20.5(2×)(CH_3COO)
11f [b]	80.4	70.7	72.9	68.4	73.1	61.7	155.0	171.1, 170.6, 169.8, 169.6(COO), 48.4(NCH), 21.1(2×), 21.0(2×)(CH_3COO), 20.5(CH_3)
12a [b]	80.9	68.6	70.8	67.2	71.8	61.0	155.4	171.9, 170.3, 170.0, 169.7(COO), 54.1(C-3′,5′), 45.6 (NCH_3), 43.2(C-2′,6′), 20.8, 20.6, 20.5 (2×) (CH_3COO)
12b [c]	82.8	69.7	74.6	68.6	76.5	60.8	156.9	54.6(C-3′,5′), 45.9(NCH_3), 43.3(C-2′,6′)
13 [b]	84.2	73.6	71.7	78.8	64.3		156.1	166.1, 165.7, 165.4(COO), 54.1(C-3′,5′), 45.7(NCH_3), 43.2(C-2′,6′)
14 [b]	101.8	69.6	50.2	74.4	59.6	69.1	157.4	135.0, 128.7, 128.0, 126.0(Ph), 101.0(CPh), 54.3, (C-3′,5′), 45.8(NCH_3), 43.8(C-2′,6′)
15 [b]	96.1	70.6	70.7	71.7	66.5	41.3	157.7	109.2, 108.6(OCO), 54.5(C-3′,5′), 46.0(NCH_3), 43.6 (C-2′,6′), 26.0, 25.8, 24.9, 24.1(CH_3)

[a] Recorded at 62.5 MHz. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$.



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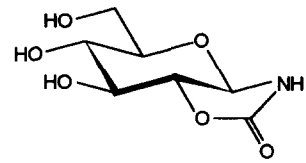

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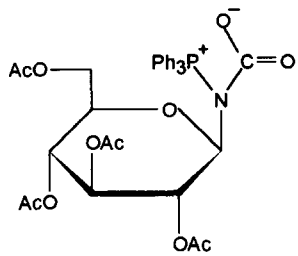

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region of δ 157.7–154.5 ppm. Additionally, signals of the protecting groups of the hydroxy functions were well established.

The reaction mechanism probably involves a reactive intermediate (e.g. **18**) —formed from the phosphinimine (e.g. **1a**) and carbon dioxide — which might play the role of the isocyanate and react with ammonium carbamate **16** before the elimination of triphenylphosphine oxide, which splits off only in the final steps.

The advantage of the phosphinimine reaction for the synthesis of sugar urea compounds is that it provides a simple and effective procedure starting from the easily available azido sugars. The method avoids the preparation of the sugar isocyanates which causes difficulties in many cases [10]. It is particularly useful for the synthesis of the acetylated glucosylurea **11g** which is an appropriate starting material for heterocyclic glucosyl compounds [4].

1. Experimental

General methods.—TLC was performed on Silica Gel F254 (E. Merck) with eluent A, 1:1 EtOAc–MeOH; and B, 3:1 Et_2O–CCl_4, unless otherwise stated; and detection by UV light at 254 nm or by charring with H_2SO_4. Dry-column flash chromatography [11] or column chromatography was effected on Silica gel 60 (E. Merck, 230–400 mesh). Optical rotations were measured with a Zeiss Polamat A polarimeter at 25°C. IR spectra were recorded in KBr discs with a Nicolet 205 FT spectrometer. NMR measurements were performed with Bruker AC-250 and Bruker AC-400 spectrometers (solutions in $CDCl_3$ or $(CD_3)_2SO$, internal Me_4Si). The ^1H signal assignment was supported by decoupling experiments. In the case of ^{13}C measurements both broadband decoupled

spectra and DETP spectra were taken. The 2D carbon–proton correlated experiments were recorded by using Bruker DISNMR software package. Microanalyses were performed in the Microanalytical Laboratory of the Institute.

General procedure for the synthesis of substituted sugar urea derivatives.—A solution of the amine (5 mmol) in dry THF (20 mL) was saturated with dry CO_2 at room temperature with stirring, while the ammonium carbamate derivative precipitated. By continuing the bubbling of CO_2 into the suspension, sugar azide (4 mmol) was added, then a solution of Ph_3P (4.2 mmol) in dry THF (10 mL) was dropped into the mixture and was allowed to react until TLC (solvent A) revealed no phosphinimine. After evaporation to dryness, the product was separated from Ph_3PO by column chromatography with Me_2CO as eluent, unless otherwise stated, yielding the following compounds (Table 1 for yields and physicochemical characteristics):

*2,3,4,6-Tetra-*O*-acetyl-*N*-(4-methylpiperazinocarbonyl)-β-*D*-glucopyranosylamine* (**11a**).—Crystallised from EtOAc. Anal. Calcd for $C_{20}H_{31}N_3O_{10}$: C, 50.73; H, 6.60; N, 8.87. Found: C, 50.89; H, 6.79; N, 8.86.

*2,3,4,6-Tetra-*O*-acetyl-*N*-(morpholinocarbonyl)-β-*D*-glucopyranosylamine* (**11c**).—Solidified by trituration with Et_2O. Anal. Calcd for $C_{19}H_{28}N_2O_{11}$: C, 49.56; H, 6.13; N, 6.08. Found: C, 50.24; H, 6.26; N, 5.41.

*2,3,4,6-Tetra-*O*-acetyl-*N*-(piperidinocarbonyl)-β-*D*-glucopyranosylamine* (**11d**).—Crystallised from Et_2O. Anal. Calcd for $C_{20}H_{30}N_2O_{10}$: C, 52.39; H, 6.60; N, 6.11. Found: C, 52.14; H, 6.70; N, 6.00.

*2,3,4,6-Tetra-*O*-acetyl-*N*-(pyrrolidinocarbonyl)-β-*D*-glucopyranosylamine* (**11e**).—Crystallised from Et_2O. Anal. Calcd for $C_{19}H_{28}N_2O_{10}$: C, 51.34; H, 6.35; N, 6.30. Found: C, 51.26; H, 6.44; N, 6.57.

*2,3,4,6-Tetra-*O*-acetyl-*N*-(diisopropylaminocarbonyl)-β-*D*-glucopyranosylamine* (**11f**).—Crystallised from Et_2O. Anal. Calcd for $C_{21}H_{34}N_2O_{10}$: C, 53.15; H, 7.22; N, 5.90. Found: C, 53.08; H, 7.26; N, 5.72.

*2,3,4,6-Tetra-*O*-acetyl-*N*-(4-methylpiperazinocarbonyl)-β-*D*-galactopyranosylamine* (**12a**).—Separated by dry-column flash chromatography with EtOAc, then 3:1 EtOAc–MeOH, then 1:1 EtOAc–MeOH; solidified by trituration with Et_2O. Anal. Calcd for $C_{20}H_{31}N_3O_{10}$: C, 50.73; H, 6. 60; N, 8.87. Found: C, 50.16; H, 6.81; N, 8.30.

*2,3,5-Tri-*O*-benzoyl-*N*-(4-methylpiperazinocarbonyl)-β-*D*-ribofuranosylamine* (**13**).—Separated by dry-column flash chromatography with 3:1 EtOAc–MeOH, then 1:1 EtOAc–MeOH; solidified by trituration with Et_2O. Anal. Calcd for $C_{32}H_{33}N_3O_8$: C, 65.40; H, 5.66; N, 7.15. Found: C, 65.08; H, 5.72; N, 6.84.

*Methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-*N*-(4-methylpiperazinocarbonyl)-α-*D*-altropyranoside* (**14**).—Separated by dry-column flash chromatography with 3:1 EtOAc–MeOH, then 1:1 EtOAc–MeOH; crystallised from Et_2O. Anal. Calcd for $C_{20}H_{29}N_3O_6$: C, 58.95; H, 7.17; N, 10.31. Found: C, 58.62; H, 7.00; N, 10.47.

*6-Amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-*N*-(4-methylpiperazinocarbonyl)-α-*D*-galactopyranose* (**15**).—Separated by dry-column flash chromatography with Me_2CO, then 1:1 Me_2CO–MeOH; solidified by trituration with Et_2O. Anal. Calcd for $C_{18}H_{31}N_3O_6$: C, 56.09; H, 8.11; N, 10.90. Found: C, 55.74; H, 8.05; N, 10.74.

*2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosylurea* (**11g**).—Dry NH_3 and CO_2 were simultaneously bubbled into dry THF (10 mL) at room temperature for 30 min to give

ammonium carbamate precipitate, then a solution of **6a** (2 mmol) in dry THF (10 mL) was added to the suspension. After dropwise addition of a solution of Ph_3P (0.58 g, 2.2 mmol) in dry THF (6 mL) stirring was continued for 24 h (monitoring by TLC, solvent MeCN). The solid was filtered and the filtrate was evaporated to dryness. The residue was subjected to column chromatography with MeCN as eluent to give pure **11g** (Table 1) which crystallised from EtOAc–Et_2O.

*N-(4-Methylpiperazinocarbonyl)-β-D-glucopyranosylamine (**11b**).*—(a) To a solution of **11a** (2.4 g, 5 mmol) in dry MeOH (25 mL) was added 2 N $NaOCH_3$/MeOH solution (0.3 mL, 0.6 mmol) and the mixture was allowed to stand at room temperature for 2 h (monitoring by TLC, solvent A). After neutralization with CO_2, and after filtration of the precipitate, the solvent was removed by distillation in vacuo and the syrupy residue was triturated with Et_2O to give crystals of **11b** (Table 1). Anal. Calcd for $C_{12}H_{23}N_3O_6 \cdot 2.5H_2O$: C, 41.14; H, 8.05; N, 11.99. Found: C, 41.21; H, 8.23; N, 11.32.

(b) A mixture of β-D-glucopyranosylamine 1,2-(cyclic carbamate) (**17**, 205 mg, 1 mmol) and *N*-methylpiperazine (115 mg, 1 mmol) in water (6 mL) was stirred for 20 min and allowed to stand overnight (monitoring by TLC, solvent A). The solution was concentrated and dried by repeated evaporation of toluene from the residue which was triturated with Et_2O. After filtration, **11b**, (268 mg, 88%) (Table 1) was obtained which was identical with the product prepared in (a).

Conventional acetylation of **11b** with Ac_2O–pyridine gave **11a**, identical with the authentic sample prepared from **6a** by the general procedure.

*N-(4-Methylpiperazinocarbonyl)-β-D-galactopyranosylamine (**12b**).*—Dry CO_2 was bubbled into a solution of **7b**, (0.61 g, 3 mmol) and *N*-methylpiperazine (0.30 g, 3 mmol) in dry DMF (7 mL) then a solution of Ph_3P (0.79 g, 3 mmol) in dry DMF (7 mL) was dropwise added and was allowed to stand for 24 h (monitoring by TLC, solvent A). After distillation of DMF in vacuo the residue was treated with CH_2Cl_2 (2×10 mL) to remove Ph_3PO. The solid was filtered, washed several times with CH_2Cl_2 to give crystals of **12b** (Table 1). Anal. Calcd for $C_{12}H_{23}N_3O_6 \cdot 2H_2O$: C, 42.22; H, 7.97; N, 12.31. Found: C, 42.09; H, 7.53; N, 11.94.

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References

[1] (a) A. Messmer, I. Pintér, and F. Szegő, *Angew. Chem.*, 76 (1964) 227–228; (b) J. Kovács, I. Pintér, A. Messmer, and G. Tóth, *Carbohydr. Res.*, 141 (1985) 57–65; (c) J. Kovács, I. Pintér, A. Messmer, G. Tóth, and H. Duddeck, *ibid.*, 166 (1987) 101–111; (d) J. Kovács, I. Pintér, G. Tóth, Z. Györgydeák, and P. Köll, *ibid.*, 239 (1993) 95–106.

[2] A. Bertho, *Ber. Dtsch. Chem. Ges.*, 63 (1930) 836–843.

[3] U. Petersen, in H. Hagemann (Ed.), *Houben-Weyl: Methoden der Organischen Chemie*, Bd. E4, Georg Thieme Verlag, Stuttgart, 1983. pp 142.

[4] B. Helferich and W. Kosche, *Ber. Dtsch. Chem. Ges.*, 59 (1926) 69–79; I. Farkas and R. Bognár, *Acta Phys. Chim. Debrecina*, 8 (1962) 55–59; CA 60 (1964) 3077g; W. E. Jensen, A. S. Jones, and G. W. Ross, *J. Chem. Soc.*, (1965) 2463–2465.
[5] A. Bertho and J. Maier, *Justus Liebigs Ann. Chem.*, 498 (1932) 50–61.
[6] R. Carrington, *J. Chem. Soc.*, (1965) 6864–6870; A. Stimac and J. Kobe, *Carbohydr. Res.*, 232 (1992) 359–365; J. Baddiley, J. G. Buchanan, L. Hodges, and J. F. Prescott, *J. Chem. Soc.*, (1957) 4769–4774.
[7] R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, (1963) 5288–5294.
[8] W. A. Szarek and J. K. N. Jones, *Can. J. Chem.*, 43 (1965) 2345–2356.
[9] F. Micheel and A. Klemer, *Adv. Carbohydr. Chem.*, 16 (1961) 85–103.
[10] I. Goodman, *Adv. Carbohydr. Chem.*, 13 (1958) 215–236. A. Piskala and F. Sorm, *Collect. Czech. Chem. Commun.*, 29 (1968) 2060–2076; T. Hassel and H. P. Müller, *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 359–360; J. Hiebl and E. Zbiral, *Justus Liebigs Ann. Chem.*, (1988) 765–774; J. Hiebl, J. Polsterer, and E. Zbiral, *Nucleosides Nucleotides*, 8 (1989) 885–886; M. Avalos, R. Babiano, P. Cintas, J. L. Jiménez, J. C. Palacios, and C. Valencia, *Tetrahedron*, 49 (1993) 2655–2675.
[11] L. M. Harwood, *Aldrichimica Acta*, 18 (1985) 25.