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^{13}C CP MAS and high-resolution ^{1}H, ^{13}C, ^{15}N NMR study of new ureido sugars, derivatives of 2-amino-2-deoxy-β-D-glucopyranose and L-amino acid

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Abstract

Ureido sugars with seven various L-amino acid ester residues were studied by means of ^{1}H, ^{13}C, and ^{15}N NMR in solution and ^{13}C CP MAS in the solid state. The chemical shifts and coupling constants in the ^{1}H, ^{13}C, and ^{15}N NMR spectra indicated that the replacement of one amino acid residue by another has no significant effect on the conformation of glucopyranose moiety. The shielding of nitrogen linked to glucose does not change, whereas the shielding of nitrogen of amino acid residues increases in the order Ala < Leu < Phe < Val < Gly and can be explained by the β-effect of the alkyl substituent at C_α. ^{13}C CP MAS spectra of **1–5** were recorded and assigned. The C-3 and C-6 carbons of sugar, the carbonyl carbons of the ureido bridge, and the carbons of the amino acid ester residues are deshielded in the solid state compared to the respective values for $CDCl_3$ solution owing to the loss of conformational flexibility and different intermolecular interactions.

Keywords: Ureido sugars; Amino acids; ^{13}C CP MAS solid state; ^{1}H NMR; ^{15}N NMR

1. Introduction

Compounds containing sugar and amino acid moieties, such as glycoproteins, are important in many biological processes. In naturally occurring products sugars are linked

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to amino acids by the N- or O-glycosidic bond; however, polyfunctionality of both partners enables other connections. Amongst various possibilities we have chosen coupling by means of an ureido bridge and synthesized a series of new ureido sugars, derivatives of 2-amino-2-deoxy-D-glucose and L-amino acid esters [1]. This paper presents the results of high-field, multinuclear NMR studies of these ureido sugars in $CDCl_3$ solution and a ^{13}C CP MAS NMR study of the solid state. The combination of solution and solid-state NMR spectroscopy provides a sensitive probe for studying the conformation and structure of these ureido sugars.

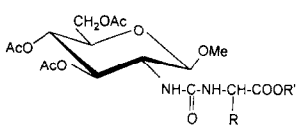
2. Results and discussion

The ureido sugars studied were derivatives of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside with the amino acid ester shown in Scheme 1.

^1H NMR spectra of ureido sugars (in diluted $CDCl_3$ solution) recorded at 500 MHz enabled the interpretation and assignment of all multiplets of sugar protons as well as those of amino acid ester residues. Some values of coupling constants were confirmed by simulation of the respective spectral region by means of the HyperNMR computer program [2]. Chemical shifts and coupling constants for sugar protons (Table 1) are typical for a peracetylated glucopyranose ring with $^4C_1$ conformation and are in agreement with those reported for arylureidoglucopyranoses [3], *O*-acetylated 2-deoxy-2-formamido-D-glucopyranoses [4], and aryl 2-acetamido-2-deoxy-β-D-glucopyranosides [5].

Comparison of chemical shifts and coupling constants for ureido sugars with those for the amino acid ester moieties and with data for 3-alkylureido sugars studied earlier [6] revealed no significant differences as far as sugar protons are concerned. The signals of N-1′–H protons (N-1′ is the nitrogen linked to the sugar) are split into doublets with $J_{2,NH}$ 7.7–7.9 Hz and appeared upfield with respect to those of N-3′–H in both series of compounds. The replacement of the alkyl group at N-3′ by the amino acid ester residue results in a downfield shift of N-3′–H proton signals, which subsequently appeared in the range δ 4.98–5.78 (in alkylureido compounds δ 4.80–5.12).

Chemical shifts and proton–proton coupling constants of amino acid ester residues in compounds **1–7** (Table 1) might be compared with those for amino acids in linear peptides. The atoms in the peptide NH–CO fragment are supposed to form a rigid, planar structure with a mainly *trans* arrangement of the NH and CO groups. Information on torsion angles around N-3–C_α and C_α–C_β can be obtained from the experimentally



Scheme 1. **1** R = H, R′ = Et (GlyOEt); **2** R = Me, R′ = Et (L-AlaOEt); **3** R = *i*-Pr, R = Et (L-ValOEt); **4** R = *i*-Bu, R′ = Et (L-LeuOEt); **5** R = Bn, R′ = Me (L-PheOMe); **6** R = CH_2COOBn, R′ = Bn (L-AspOBn); **7** R = CH_2CH_2COOBn, R′ = Bn (L-GluOBn).

Table 1
^{1}H NMR data ($CDCl_3$, δ in ppm, J in Hz) for ureido sugars **1**–**7** [a]

Atom	1	2	3	4	5	6	7
H-1	4.40 d	4.40 d	4.38 d	4.44 d	4.37 d	4.36 d	4.40 d
$J_{1,2}$	8.2	8.2	8.2	8.2	8.0	8.2	8.3
H-2	3.60 ddd	3.60 ddd	3.52 ddd	3.64 ddd	3.54 ddd	3.58 ddd	3.62 ddd
$J_{2,NH}$	7.9	7.9	7.7	8.3	7.9	7.9	
$J_{2,3}$	10.4	10.3	10.3	10.3	10.3	10.3	9.9
H-3	5.13 dd	5.13 dd	5.12 dd	5.16 dd	5.12 dd	5.12 dd	5.13 dd
$J_{3,4}$	9.3	9.3	9.3	9.3	9.3	9.3	8.9
H-4	5.06 dd	5.04 dd	5.05 dd	5.04 dd	5.02 dd	5.03 dd	5.02 dd
$J_{4,5}$	9.5	9.5	9.7	9.6	9.7	9.3	8.9
H-5	3.67 ddd	3.66 ddd	3.66 ddd	3.69 ddd	3.64 ddd	3.64 ddd	3.67 ddd
$J_{5,6a}$	4.8	4.8	4.8	4.9	4.9	4.8	4.7
$J_{5,6b}$	2.6	2.6	2.6	2.3	2.6	2.6	2.6
H-6a	4.25 dd	4.34 dd	4.28 dd	4.26 dd	4.25 dd	4.25 dd	4.28 dd
$J_{6a,6b}$	12.3	12.3	12.3	12.3	12.3	12.3	12.1
H-6b	4.13 dd	4.15 dd	4.12 dd	4.15 dd	4.12 dd	4.13 dd	4.11 dd
N-1′–H	4.69 d	4.47 d	4.53 d	4.95 d	4.55 d	4.59	5.00
N-3′–H	5.45 t	5.29 d	5.70 b	5.36 d	5.26 d	5.78 d	5.57 d
$J_{\alpha,NH}$	4.8, 5.8	7.3	broad	8.1	6.6	7.5	8.1
H_α	3.82, [b] 4.02	4.40	4.28	4.41	4.70	4.74	4.51
$J_{\alpha,\beta}$		7.1	4.6	6.7	5.9, 6.2	4.8, 4.8	7.5, 7.6
H_β		1.35	2.10	1.47, 1.59	3.03, 3.10	2.88, 3.03	2.01, 2.17
$J_{\beta,\beta'}$				18	14	17	14
H_γ			0.88, 0.92	1.47			2.34, 2.39 [c]
$J_{\beta,\gamma}$			6.9	5.5			6.8, 8.0
H_δ				0.91, [d] 0.93			

[a] Chemical shifts for ester group OMe, OEt, OBn are not given.
[b] $^2J_{\alpha,\alpha'}$ 18.2 Hz.
[c] $J_{\gamma,\gamma'}$ 13 Hz.
[d] $J_{\gamma,\delta}$ 5.9 Hz.

calibrated angular dependence of vicinal coupling constants [7]. However, NMR spectra of peptides were measured almost exclusively in H_2O/D_2O or DMSO-d_6 solution; there are no NMR data available for $CDCl_3$. The spectra of ureido sugars **2** and **4** were, therefore, also recorded in Me_2SO. The significant upfield shift of H_α (0.26–0.28 ppm) and H_β (0.09–0.15 ppm) signals can be noticed compared to the respective values of chemical shifts for $CDCl_3$ solutions. The values of $J_{NH\alpha}$ were approximately 6% higher in Me_2SO than in $CDCl_3$. In none of the cases was $J_{NH\alpha} > 10$ Hz achieved (i.e., the maximum of the Karplus curve, which indicates a relatively rigid conformation) and the values within 7.8–8.6 Hz have a three-fold degeneracy in terms of solution for the torsion angle N-3′–C_α [7]. The favoured conformations around the C_α–C_β bond are three staggered states $g+$, t, and $g-$ with non-equivalent protons H_β and $H_{\beta'}$. A further problem to be answered is: does the molecule exist in a single conformation or flip between two or three of them? Sensitivity of NMR parameters to changes of solvent suggests that amino acid residues bound to ureido sugars exist in solution in more than one conformational state.

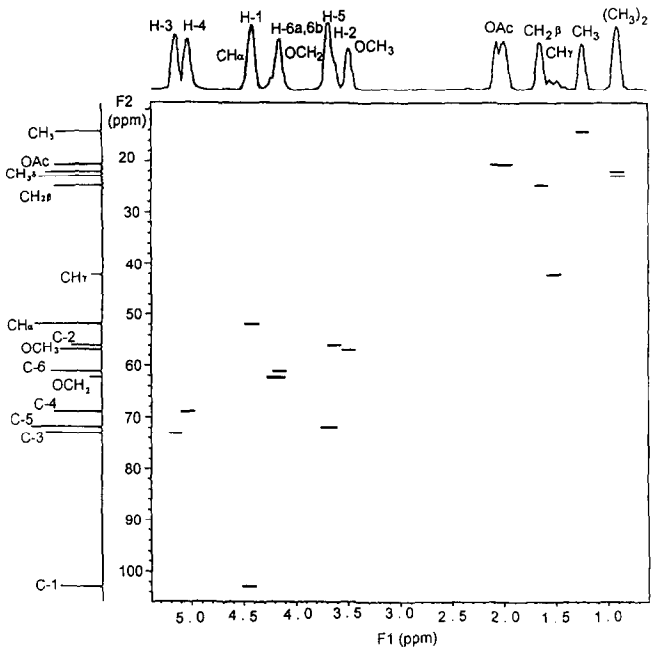


Fig. 1. $^{1}H-^{13}C$ HETCOR spectrum of **4**.

The non-labile protons of amino acid residues form complicated spin systems due to the presence of the chiral carbon atom C_{α}. An interesting feature is the non-equivalence of methylene group protons in glycine resulting in a difference in the chemical shifts of $CH_{2\alpha}$ protons and $\delta\ H_{\alpha} - \delta\ H_{\alpha'} = 0.20$ ppm. Local diastereotopicity in other amino acid ester moieties is generated by chiral centres. In the spectra of **3** and **4**, with a $CH(CH_3)_2$ group, the difference in chemical shifts of methyl protons is 0.04 and 0.02 ppm, respectively, because the distance from the chiral C_{α} carbon increases.

Diastereotopic methylene protons $CH_{2\beta}$ in **5–7** give an ABC pattern of spin–spin coupling with neighbouring CH_{α} and N-3′ protons. The difference $\delta\ H_{\beta} - \delta\ H_{\beta'}$ is 0.07 to 0.15 ppm and geminal coupling constants $J_{\beta,\beta}$, from 14 to 17 Hz.

The overlapping of C_{α}–H and ester–OCH_2 signals with those of sugar H-1, H-6a,b protons caused difficulties in the chemical shift assignment, the 2D HETCOR spectra were, therefore, recorded for compounds with Leu (**4**) and Glu (**7**) residues. The interpretation of two-dimensional spectra revealed that the most downfield signal in the ^{13}C NMR spectra (excluding anomeric carbon C-1) should be ascribed to C-3 and the order of chemical shifts of sugar carbon signals in the range 75–60 ppm should be: C-3 > C-5 > C-4. It is highly probable that the same order is also valid in the ureido sugars with alkyl substituents and the assignments [6] should be corrected, i.e., the positions of C-3 and C-5 resonances interchanged (see Fig. 1).

^{15}N NMR spectra were recorded with the INEPT technique and in the typical spectra (not shown) of ureido sugars the two doublets appeared with J_{NH} in the range -88.7 to -90.1 Hz. The chemical shift of N-1′, linked to D-glucose is ca. -300 ppm and is

essentially unchanged with substitution of another amino acid residue at N-3′ (Table 2). The same values for nitrogen chemical shifts and $J_{N,H}$ show that the conformation within the fragment, glucose–N-1′–H–CO-, remains the same in the whole series of compounds **1–7**. The ^{13}C chemical shifts of C-2, as well as the value of J_{NH} established from the ^{15}N NMR spectra, were indicative of the *Z,Z* configuration of these series of compounds as discussed in detail in a previous paper [6]. The values of coupling constants for N-3′–H are slightly higher than those for N-1′–H. The magnitude of $^{1}J_{N,H}$ usually increases with the increasing *s* character of the N–H bond [8], and the changes in $^{1}J_{N,H}$ of N-3′–H reflect charge distribution within N-3′–H–C_α resulting from the proximity of the ester $COOR_1$ group.

Chemical shifts of N-3′ nitrogens are more variable and can be compared with the values for *N*-acetyl derivatives of amino acids. Usually, in peptide-type linkages, the highest shieldings are observed for glycine units with R = H. In the ureido sugars **1–5** the effects of substituent R are analogous to those observed in *N*-acyl and *N*-carbobenzyloxy amino acids [9] (Table 2), and could be explained by the β-effect of the alkyl group R at C_α (see Scheme 1). The shielding of nitrogen N-3′ increases in the order Ala < Leu < Phe < Val < Gly in all three series of compounds considered (Table 2) although in amino acids whose amino groups are linked to carbamate- or ureido-type structures the shieldings are 20–30 ppm higher than those in *N*-acyl amide type.

It was of interest to study our compounds without any solvent, by means of a ^{13}C CP MAS NMR technique. Solid ureido sugars were powdered, placed in a rotor, and spun at

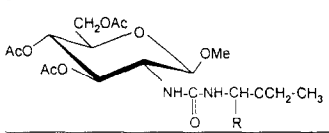
Table 2
^{15}N NMR chemical shifts ($CDCl_3$, δ in ppm, ref. CH_3NO_2) of amide [9] and carbamate [9] of amino acids and ureido sugars **1–5**

R	Amide [a] N_α (N-3′)	Carbamate [b] N_α (N-3′)	Glucopyranosyl ureas		Compound
			N-3′	N-1′	
–H	−271.3	−303.5	−307.58 (90.14) [c]	300.18 (89.43)	**1**
$-CH_3$	−253.8	−289.1	−292.25 (90.04)	−300.24 (89.28)	**2**
$-CH(CH_3)_2$	−261.9	−295.2	−298.88 (89.07)	−299.25 (88.21)	**3**
$-CH_2CH(CH_3)_2$	−258.3	−291.7	−294.13 (89.84)	−300.12 (89.23)	**4**
$-CH_2C_6H_5$	−259.2	−292.5	−296.91 (89.94)	−300.12 (89.13)	**5**
			−294.1 (88.7)	−301.2 (88.7)	**8** [d] [1]

[a] $CH_3-CO-NH-\underset{\displaystyle R}{\underset{|}{CH}}-COOH$.

[b] $C_6H_5-O-CO-NH-\underset{\displaystyle R}{\underset{|}{CH}}-COOMe$.

[c] $J_{N,H}$ in parentheses in Hz.

[d]


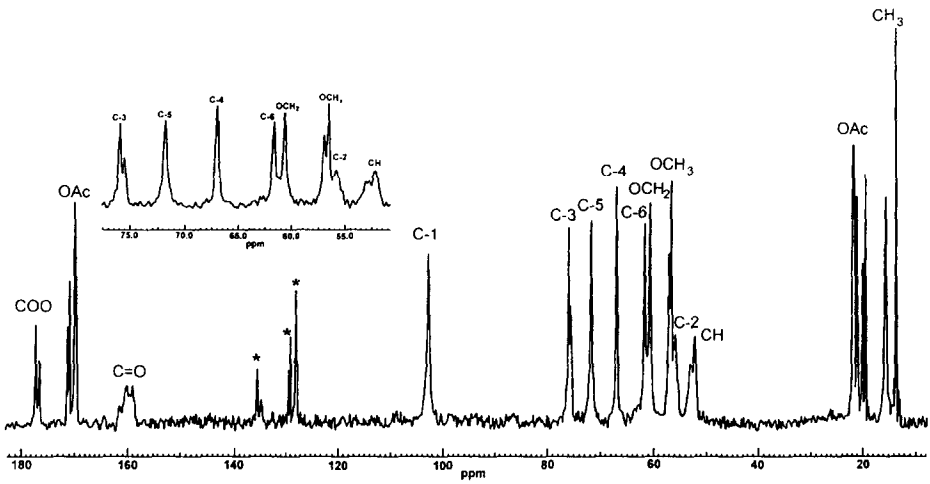


Fig. 2. ^{13}C CP MAS spectrum of compound **2** (*, spinning side band).

3.0–3.2 kHz. The spinning speed of ca. 3 kHz was enough to circumvent spinning side bands, in several cases the spectra were repeated with the rotation speed increased to 3.6–3.8 kHz or recorded with the dipolar dephased pulse sequence (50 μs delay) which exposes carbons not bound to hydrogen atoms, i.e., the carbonyl carbons. The solid-state CP MAS spectrum of **2** is shown in Fig. 2 and the spectrum of **5** in Fig. 3.

The signals of carbons linked to nitrogen, N–CO–N, N-1′–C-2, N-3′–C_α, are broader and exhibit residual splitting (see Fig. 2, the expanded region of sugar carbons) because both the ^{13}C–^{14}N dipolar and ^{14}N quadrupolar interaction cannot be eliminated simultanously by magic-angle spinning. These signals can therefore be easily distinguished from other carbon signals (Table 3). The structure of the D-glucopyranose ring with $^4C_1$ conformation is rigid and no significant change of carbon shieldings has been observed: with the exception of C-6, because in solution three staggered conformations, *gg*, *gt*, and *tg*, around the C-5–C-6 bond are possible. Frozen rotation around the C-5–C-6 bond of D-glucose results in deshielding of the C-6 carbons (−1.0 to −2.2 ppm) because of different orientation and interaction of the $-CH_2-OAc$ group.

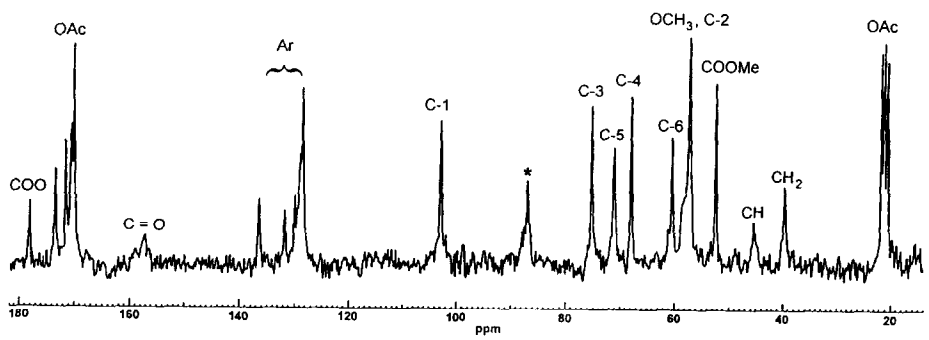


Fig. 3. ^{13}C CP MAS spectrum of compound **5** (*, spinning side band).

Table 3
^{13}C NMR chemical shifts of ureido sugars **1–5** in solid state and (in parentheses) the differences Δ (ppm) = $\delta_{liquid} - \delta_{solid}$ [a]

Atom	1	2	3	4	5
C-1	103.4	102.7	103.8	102.7	102.8
C-2	54.5	55.8	54.2	57.1	57.1
C-3	71.5	75.9 (−2.7)	75.7 (−2.6)	74.9 (−1.7)	75.2 (−2.0)
C-4	69.7	66.9	69.5	67.7	67.8, 71.0
C-5	71.5	71.7	71.3	72.6, 71.4	71.0
C-6	60.7 (−1.7)	61.6 (−1.0)	63.3 (−1.0)	61.2 (−1.2)	60.3 (−2.2)
OMe	58.3	56.5	59.8 (−2.8)	57.1	57.1
CH_3COO	171.15, 170.4	171.3, 170.9	169.8, 169.5	171.6, 170.6	170.4, 169.9
	169.7	169.8	169.0	169.7	
CH_3COO	21.2, 20.6	21.9, 21.6	20.7, 20.4	21.6, 21.0	21.6, 21.11
	19.6	21.0, 19.9		20.3, 19.5	20.5
		19.4			
NCON	160.6 (−2.5)	159.8 (−2.5)	159.1 (−1.5)	159.0 (2.0)	159.0 (−2.0)
OCH_2	55.5	60.6	61.4	63.0, 61.0 (−1.8)	52.3
CH_3	14.4	13.5	14.5	13.4, 13.1	
C_α	43.5 (−1.2)	52.1 (−3.1)	60.0 (−2.0)	53.3 (−1.5)	57.1 (−2.9)
C_β		15.5 (−3.6)	30.0 (1.3)	26.1 (−2.2)	39.6 (−1.2)
C_γ			20.0, 18.4	42.8	
C_δ				24.1, 23.0	
$C_{aromat.}$					136.4, 129.8
					128.3
$COO_{ester.}$	172.8	177.2, 176.5	175.4	176.6, 175.9	178.0

[a] $\Delta < 1$ ppm are neglected.

Molecular modelling [2] shows that an intermolecular hydrogen bond is possible between N-3–H and the carbonyl oxygen of the acetyl group at C-3. The deshielding of C-3 (−1.7 to −2.6 ppm) is probably connected with the changing mode of association: instead of internal H-bonds both NH groups in solids are involved in intermolecular H-bonds. The deshielding of the N-1′–CO–N-3′ carbonyl carbon (−1.5 to 2.5 ppm) is mainly due to the strong intermolecular interactions in the solids, i.e., hydrogen bond formation by NH and CO groups, whereas in diluted $CDCl_3$ solutions (0.05 M) the contribution from intermolecular hydrogen bonding can be neglected. X-ray data are not available on the structure of ureido sugars but comparisons can be drawn with ureas having alkyl substituents. The X-ray diffraction investigation of unsymmetrical *N,N′*-dialkylureas showed that molecules are linked together by intermolecular [10] as well as both intra- and inter-molecular [11] hydrogen bonds NH · · · O=C.

^{13}C chemical shifts of the carbon of carbonyl groups in peptides containing glycine residues in the solid state give a linear relationship [12] with hydrogen bond lengths (determined from X-ray studies). A decrease of the N · · · O distance results in a downfield shift of the CO signal. The ^{13}C chemical shift of the carbon of the carbonyl group of glycine in the ureido sugar derivative **1** is δ 172.8 (Table 3); the same value has been measured for polyglycine with the N · · · O hydrogen bond as long as 2.72 Å.

It can be supposed, therefore, that the molecules of ureido sugar **1** are linked by relatively short and strong hydrogen bonds.

Deshielding of C_α (−1.2 to −3.1 ppm) is observed in the spectra of solid compounds **1–5**, as well as significant changes of shielding (+1.3 to −3.6 ppm) of the proximal carbon C_β. These effects support the conclusion that this is a conformationally flexible fragment of the molecule.

In the ^{13}C CP MAS spectrum of DL-valine [13] the two methyl carbons were not chemical shift equivalent, but in the L-isomer of valine four methyl peaks were observed at δ 18.5, 19.6, 20.9, and 22.5. In the L-valine residue linked to the ureido sugar **3** the signals of methyl groups appeared at δ 18.4 and 20.0, separated by 1.6 ppm. Methyl carbons of the $CH(CH_3)_2$ fragment of **4** appeared at δ 23.0 and 24.1 and the separation of signals is 1.1 ppm because the distance to chiral carbon C_α increases. Methyl and carbonyl carbons from three acetyl groups at the sugar ring give well-resolved signals (Figs. 2 and 3) but in the spectra of **2** and **4** these signals exhibit additional splittings.

The splitting of some carbon signals (Table 3), arising from chemical shift difference, reflects differences in crystal packing and cannot be explained without X-ray data (i.e., the possible existence of an asymmetric unit cell or the coexistence of two different crystalline forms).

3. Experimental

Ureido sugars were synthesized from methyl 3,4,6-tri-*O*-acetyl-2-deoxy-(4-nitrophenoxycarbonylamino)-β-D-glucopyranoside and amino acid methyl, ethyl, or benzyl esters according to the described procedures [1]. The following ureido sugars were prepared: *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-glycine ethyl ester (**1**), *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-L-alanine ethyl ester (**2**), *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-L-valine ethyl ester (**3**), *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-L-leucine ethyl ester (**4**), *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-L-phenylalanine methyl ester (**5**), *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-L-aspartic acid dibenzyl ester (**6**), *N*-(methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside)-*N'*-carbamoyl-L-glutamic dibenzyl ester (**7**).

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-500 spectrometer for 0.05 M solutions in $CDCl_3$. ^{15}N NMR spectra were measured on a Bruker AM-500 spectrometer at 50.7 MHz using INEPT pulse sequence, chemical shifts were measured for 0.4 M solutions in $CDCl_3$ and referenced to CH_3NO_2.

^{13}C NMR spectra of solids were recorded on a Bruker MSL-300 spectrometer at 75.5 MHz using magic-angle spinning and cross-polarization techniques. Powdered samples were placed in a 7-mm cylindrical ZrO_2 rotor and spun at 3–4 kHz; 500–2100 scans with a contact time of 5 ms, a repetition time of 10 s, and spectral width of 20 kHz were accumulated. Chemical shifts were calibrated indirectly through the glycine CO signal observed at δ 176.3 relative to TMS.

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