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PROTECTION OF THE AMINO GROUP OF AMINO SUGARS BY THE ACYLVINYL GROUP: PART I, GLYCOSIDE FORMATION BY THE FISCHER REACTION

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ABSTRACT

2-Deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]- (**1**) and 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (**3**), prepared in almost quantitative yields from the appropriate 3-alkoxy-2-alkoxycarbonylacrylic ester and 2-amino-2-deoxy-D-glucose hydrochloride, were used as *N*-protected derivatives in the preparation of glycosides by the Fischer procedure. Glycosidation of **1** with boiling methanolic hydrogen chloride afforded a mixture of methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]-α- (**7α**) and -β-D-glucopyranoside (**7β**), and minor amounts of methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]-α-D-glucofuranoside (**18**); **7α** was easily isolated (55% yield). Using Amberlyst-15 (H^+) resin as catalyst, the proportion of the furanoside **18** was higher and 21% could be isolated. Reaction of **3** with hot ethanolic hydrogen chloride afforded a good yield of ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranoside. On the other hand, attempted glycosidations of 2-deoxy-2-[(2,2-diacetylvinyl)amino]-α-D-glucopyranose under similar conditions were unsuccessful. The 2,2-diacylvinyl group could be removed selectively under non-acidic conditions using chlorine, ammonia, or Amberlite IRA-400 (HO^-) resin.

INTRODUCTION

Following the reports by Dane and co-workers[1], the acylvinyl group has often been used to protect the amino group of amino acids during the syntheses of peptides and penicillin derivatives. We have described[2–4] the preparation of several 2-(2-acylvinylamino)-2-deoxy-α-D-glucopyranoses (for example, **11–13**) and their use in simple syntheses of 1,3,4,6-tetra-*O*-acetyl- and 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose. Compounds **11–13**, and their analogues, do not mutarotate, and afford exclusively α-tetra-acetates; apparently, the *N*-(2-acylvinyl) group

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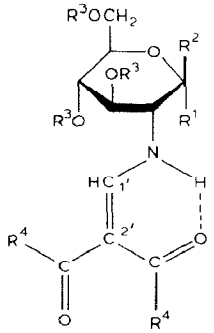
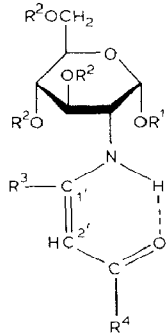
reinforces the anomeric effect, and this property could be useful in preparing other derivatives of 2-amino-2-deoxy-α-D-glucose. In order to further explore the potential of the acylvinyl group as a protecting group, we have investigated the behaviour of several 2-deoxy-2-(2,2-diacylvinylamino)- (**1, 3,** and **5**) and 2-(2-acylvinylamino)-2-deoxy-α-D-glucopyranoses (**11–13**) under the conditions of the Fischer glycoside synthesis.

RESULTS AND DISCUSSION

Preparation of (2-acylvinylamino)glycoses. — Compounds **1, 3,** and **5** were obtained by treating an aqueous solution of 2-amino-2-deoxy-D-glucose hydrochloride and sodium carbonate with the appropriate 3-alkoxy-2-alkoxycarbonylacrylic ester or with 3-acetyl-4-ethoxy-3-buten-2-one (ethoxymethyleneacetylacetone); 90–98% yields of crystalline products were obtained. When the reactions were performed in methanolic triethylamine[5], the yields were slightly lower. Acetylation of **1, 3,** and **5** afforded high yields of the corresponding tetra-acetates **2, 4,** and **6**.

The analytical and spectroscopic data (Tables I and II) of **1–6** were consistent with the assigned structures. The absorptions due to the 2,2-diacylvinylamino group





1 R^1 = OH, R^2 = R^3 = H, R^4 = OMe
2 R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = OMe
3 R^1 = OH, R^2 = R^3 = H, R^4 = OEt
4 R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = OEt
5 R^1 = OH, R^2 = R^3 = H, R^4 = Me
6 R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = Me
7α R^1 = R^4 = OMe, R^2 = R^3 = H
8α R^1 = R^4 = OMe, R^2 = H, R^3 = Ac
7β R^1 = R^3 = H, R^2 = R^4 = OMe
8β R^1 = H, R^2 = R^4 = OMe, R^3 = Ac
9 R^1 = R^4 = OEt, R^2 = R^3 = H
10 R^1 = R^4 = OEt, R^2 = H, R^3 = Ac

11 R^1 = R^2 = H, R^3 = R^4 = Me
12 R^1 = R^2 = R^3 = H, R^4 = Ph
13 R^1 = R^2 = H, R^3 = Me, R^4 = Ph
14 R^1 = Me, R^2 = R^3 = H, R^4 = Ph
15 R^1 = Me, R^2 = Ac, R^3 = H, R^4 = Ph
16 R^1 = R^3 = Me, R^2 = H, R^4 = Ph
17 R^1 = R^3 = Me, R^2 = Ac, R^4 = Ph

of these compounds were similar to those for simple 2-alkoxycarbonyl-3-alkylaminoacrylic esters[6] and 3-acetyl-4-alkylamino-3-buten-2-ones[7]; the presence of the chelate structure was indicated by the low stretching-frequencies of the bonded NH and C=O groups, the large δ values of the signals for the NH protons, and the large $J_{NH,1'}$ couplings. The splitting of the carbonyl bands observed in the diesters **1–4** is attributed, as in 2-alkoxycarbonyl-3-alkylaminoacrylic esters[6], to the restricted rotation around the bond joining C-2′ and the free CO_2R group, which allows the existence of *s-trans* (represented in the formulae) and *s-cis* rotational isomers. In spite of this fact, the relatively high ν(C=O) value of the free CO_2R (*cf.* ~1690 cm^{-1} for the *E*-form of 3-alkylaminoacrylic esters[8]) indicated weak conjugation with the rest of the unsaturated system, and the group is probably twisted out of the plane of the chelate ring[6a]. The presence of rotational isomers was not observed for **5** and **6**, and the i.r. spectra showed three bands in the double-bond region; that (~1655 cm^{-1}) of highest frequency, which had weak or medium intensity in the i.r. and strong intensity in the Raman spectra, was assigned as a symmetrical mixed vibration with a large component of the ν(C=O) of the carbonyl in the *s-trans* conformation, *trans* to the amino group. The second band (~1630 cm^{-1},

TABLE I
U.V. AND I.R. ABSORPTIONS OF COMPOUND **1–10**

Compound	λ_{max}, *nm (log* ε*)*[a]		ν *(cm^{-1})*[b]			
			ν*(N-H)*	ν(C=O)[c]		*C=C–NH*[d]
				Free	*Bonded*	
1	278	(4.26)	[e]	1700	1670s 1660s	1615s
2[f]	277	(4.17)	3265vw	1732s 1698s	1665s 1657s	1612s
3	280	(4.36)	[e]	1691s	1669s	1618s
4			3265vw	1705s	1656s	1606s
5	262 294	(4.17) (4.28)	[e]	1649m	1615vs	1569s
6	249 288	(3.80) (4.16)	3185vw,b	1660sh	1630vs	1590s
7α[g]	278	(4.24)	[e]	1709s 1688s	1660vs 1648sh	1605s
8α	277	(4.11)	3270vw	1720vs	1660s	1610s
7β	288	(3.98)	[e]	1680vs	1630vs	1595s
8β			3250vw	1700s	1660s	1605s
9	282	(4.36)	3280sh	1720sh 1691vs	1666s 1638s	1611s
10	236 282	(3.88) (4.24)	3260vw	1706s 1696s	1665s	1608s

[a]In ethanol. [b]For KBr pellets unless otherwise indicated. [c]Of the 2,2-diacylvinyl group. [d]Assigned to a mixed ν(C=C) + δ(N–H) mode; disappears on *N*-deuteration. [e]Obscured by the ν(O–H) absorption. [f]I.r. in carbon tetrachloride solution. [g]I.r. in methyl sulphoxide solution.

TABLE II

^{1}H-N.M R. DATA[a] (δ, p.p.m.; J, Hz) FOR **1–10**

Compound	*NH*	*H-1'*	*R*[4]	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*2H-6*	*OAc*	*MeO-1*
1[b,c]	9.30dd,br $J_{NH,1'}$ 13.2 $J_{NH,2}$ 8.4	8.15d	3.56s, 3.61s	5.13d $J_{1,2}$ 3.5							
2[c]	9.10dd,br $J_{NH,1}$ 13.2 $J_{NH,2}$ 8.3	7.95d	3.70s, 3.77s	6.25d $J_{1,2}$ 3.5		5.40t $J_{2,3} \cong J_{3,4}$ 8.5	5.11t $J_{4,5}$ 8.5			2.03s, 2.04s, 2.07s, 2.25s,	
3[b]	9.10dd,br $J_{NH,1'}$ 14.0 $J_{NH,2}$ 9.0	8.02d	1.21t,1.30t, 4.05q, 4.12q J 7.5	5.15d $J_{1,2}$ 3.5							
4	9.06dd,br $J_{NH,1'}$ 13.5 $J_{NH,2}$ 9.5	7.98d	1.26t,1.30t, 4.14q,4.21q J 7.5	6.25d $J_{1,2}$ 3.9	3.65dt $J_{2,3}$ 9.5	5.35t $J_{3,4}$ 9.5	5.21t $J_{4,5}$ 9.5		3.95–4.45m	2.00s, 2.02s, 2.06s, 2.23s	
5[b]	10.80dd,br $J_{NH,1}$ 13.5 $J_{NH,2}$ 8.7	8.12d	2.32s, 2.45s	5.13d $J_{1,2}$ 3.0							
6	10.90t,br $J_{NH,1'}$ 12.0 $J_{NH,2}$ 10.0	7.70d	2.32s, 2.43t	6.28d $J_{1,2}$ 3.6	3.74dt $J_{2,3}$ 10.0	5.42t $J_{3,4}$ 9.75	5.14t $J_{4,5}$ 9.3		3.95–4.45m	1.99s, 2.02s, 2.06s, 2.27s	

7α[b,c]	9.10dd,br $J_{NH,1'}$ 14.6 $J_{NH,2}$ 7.0	8.02d	3.59s, 3.64s	4.76d $J_{1,2}$ 2.7						3.33s
8α[d]	8.98dd,br $J_{NH,1'}$ 14.0 $J_{NH,2}$ 10.7	7.90d	3.71s, 3.79s	4.89d, $J_{1,2}$ 3.5	3.49sx $J_{2,3}$ 9.9	5.32t $J_{3,4}$ 9.9	5.05t $J_{4,5}$ 9.9	4.03ddd $J_{5,6}$ 4.5 $J_{5,6'}$ 2.1	4.11dd 4.32dd $J_{6,6'}$ −12.3	1.98s, 2.03s 2.09s	3.49s
7β[b]	9.05dd,br $J_{NH,1'}$ 14.3 $J_{NH,2}$ 7.5	7.91d	3.57s, 3.65s	4.48d $J_{1,2}$ 8.0							3.38s
8β	9.10dd,br $J_{NH,1'}$ 14.0 $J_{NH,2}$ 9.5	7.95d	3.71s, 3.78s	4.48d $J_{1,2}$ 8.0	3.32q $J_{2,3}$ 9.0	5.32t $J_{3,4}$ 9.0	5.10t, $J_{4,5}$ 9.0	4.10–4.40m		2.04s, 2.05s 2.10s	3.52s
9	8.99dd,br $J_{NH,1'}$ 14.6 $J_{NH,2}$ 7.0	7.96d	1.19t,1.22t, 4.01q,4.12q *J* 7.5	4.85d $J_{1,2}$ 2.8							1.22t[e] 4.12q *J* 7.5
10	8.98dd,br $J_{NH,1'}$ 14.0 $J_{NH,2}$ 9.0	7.88d	1.32t,1.37t, 4.19q,4.25q *J* 7.8	4.98d $J_{1,2}$ 3.3	3.52sx $J_{2,3}$ 10.0	5.36t $J_{3,4}$ 10.0	5.04t $J_{4,5}$ 10.0			2.05s, 2.06s, 2.12s	1.37t,[e] 4.25q *J* 7.8

[a]At 90 MHz in $CDCl_3$ unless otherwise stated. [b]In Me_2SO-d_6. [c]At 60 MHz. [d]At 360 MHz. [e]EtO-1.

strong in the i.r. and weak in the Raman spectra) is the corresponding asymmetrical mode having a large component of the ν(C=O) of the intramolecularly bonded carbonyl group in the *cis,s-cis* disposition. These two bands were insensitive to *N*-deuteration. The third band (~1580 cm^{-1}) was sensitive to deuteration and was assigned as a mixed ν(C=C) + δ(N-H) vibration. No band was observed in the range 1680–1655 cm^{-1} which could be attributed[9] to the *trans* carbonyl in the *s-cis* conformation. All these groups seem to be strongly conjugated and mechanically coupled, and, therefore, lying rigidly in one plane. An X-ray crystallographic study[10] of **5** has confirmed the structure and conformation assigned, and indicated that the C=C–NH group and the acetyl group *trans* to the amino function are coplanar, whereas the chelated acetyl group lies in a different plane twisted 7° from the former.

The α-D configurations were deduced from the high, positive, optical rotations, the $J_{1,2}$ values, and, for the tetra-acetates **2, 4,** and **6**, from the position of the AcO-1 signal at δ ~2.25. The ring size and anomeric configuration of **6** was confirmed by its conversion into 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride as described below. Compounds **1, 3,** and **5** did not mutarotate and appear to have the same strong preference for the α-D configuration as other *N*-(acylvinyl) derivatives of 2-amino-2-deoxy-D-glucose[2–4].

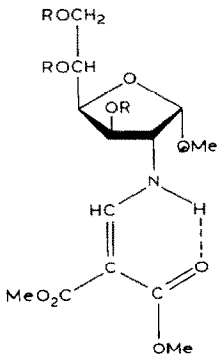
The alkyl 2-[(2,2-diacylvinyl)amino]-2-deoxy-α- and -β-D-glucopyranosides **7** and **9**, which were expected to be products of the glycosidation reactions described below, were unequivocally synthesised by reaction of the appropriate alkyl 2-amino-2-deoxy-α- or -β-D-glucopyranoside hydrochloride and 3-alkoxy-2-alkoxycarbonylacrylic ester. Acetylation then afforded the corresponding triacetates **8α** and **10**. The spectroscopic properties (Tables I and II) of **7–10** were consistent with the assigned structures.

The 2-[(2-acylvinyl)amino]-2-deoxy-α-D-glucopyranoses **11–13** were prepared as previously described[2–4], and **14** and **16** were synthesised by reaction of methyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride with benzoylacetaldehyde and 1-phenyl-1,3-butanedione, respectively, in methanol–triethylamine. Acetylation of **14** and **16** afforded the corresponding triacetates **15** and **17**.

Fischer reactions. — With boiling, methanolic 2.5% hydrogen chloride, **1** gave (t.l.c.) methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl) amino]-α-D-glucopyranoside (**7α**, major product), its anomer (**7β**), and minor amounts of methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]-α-D-glucofuranoside (**18**). At equilibrium (5 h), no **1** remained and the ^{1}H-n.m.r. spectrum of the crude crystalline mixture of glycosides indicated a ratio of ~7:3 for **7α** and **7β**. Fractional crystallisation of the mixture gave >55% of **7α**. Acetylation of the crude glycosidation product, followed by column chromatography, afforded **8α** (61%) and **8β** (25%).

Methyl glycosidation of **1** in the presence of Amberlyst-15 (H^+) resin was slow, and **7α** and **18** were the main products (t.l.c.). After 24 h, **1** was still present, and column chromatography afforded **18** (25%) and a mixture (35%) of **7α** and **7β** in the ratio ~2:3 (^{1}H-n.m.r. data); 15% of **1** was recovered.

The furanoside **18** consumed 1 mol of periodate and liberated 1 mol of formaldehyde, but no formic acid, in accordance with the furanose structure. Likewise, the pyranoside **7α** consumed 1 mol of periodate, but no formic acid or formaldehyde was liberated, indicating that the 2,2-diacylvinylamino group does not interfere in the normal periodate oxidation.



18 R = H
19 R = Ac

The furanoside **18** was almost quantitatively converted into the thermodynamically more stable pyranoside **7α** when heated with methanolic hydrogen chloride. The $J_{1,2}$ values (~5 Hz) of **18** and its triacetate **19** did not allow determination of the anomeric configuration[11], but the $[\alpha]_{5461}$ values (+170° for **18**, and +204° for **19**) indicated the α-D configuration, and this assignment was confirmed by conversion of **18** into known[12] methyl 2-amino-2-deoxy-α-D-glucofuranoside as described below.

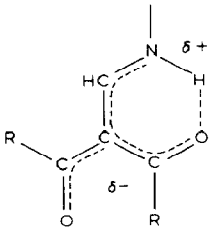
Treatment of **3** with boiling ethanolic hydrogen chloride gave (t.l.c.) ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**9**) and minor amounts of two other products which, on the basis of the similarity of their chromatographic properties to those of **7β** and **18**, were considered to be the analogous ethyl glycosides. After reaction for 6 h, 90% of a glycoside mixture was obtained from which 66% of **9** was isolated and converted into its triacetate **10**.

Compound **1** and **3** are glycosidated more slowly than other *N*-protected 2-amino-2-deoxy-D-glucoses (*cf.* 3 h for the methyl glycosidation of the *N*-acetyl derivative under similar conditions[13]) and no reaction occurred at room temperature.

Glycosidation of **3** with boiling methanolic hydrogen chloride took place with concomitant transesterification, and ~50% of **7α** was isolated from the complex mixture of products.

By contrast with the vinylogous urethanes, the vinylogous amides were not suitable substrates for glycosidation reactions. For example, when **5** was heated with methanolic hydrogen chloride, the only product was 2-amino-2-deoxy-D-glu-

cose hydrochloride. Compounds **11–13** behaved similarly. This remarkable difference in reactivity between the two types of derivatives can be attributed to the different degree of polarisation inside the 2,2-diacylvinylamino system that may be represented by the average structure **20**. The amino function of the almost planar and highly delocalised group **20** of **5**, and probably that of the similar groups of **11–13**, bear a high positive charge which effectively inhibits acid-catalysed glycosidation. This effect is not so pronounced in the less delocalised derivatives **1** and **3** which react similarly, but more slowly, than the usual acylamino sugars.



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Removal of the 2,2-diacylvinyl group. — Three procedures *A–C* (Table III), which avoided acid conditions, were used. Procedure *A* employed chlorine, as used in peptide chemistry[14] (60–85% yields of hydrochlorides). Procedure *B* involved ammonia in aqueous acetone, and probably a transamination reaction. An equilibrium was attained in which an appreciable amount of the starting material was still present. The yields of products, usually after chromatography, were variable, as illustrated by the two examples included in Table III. The second product of the reaction, namely, methyl 3-amino-2-methoxycarbonylacrylate, was isolated from

TABLE III

REMOVAL OF THE *N*-(2,2-DIACYLVINYL) PROTECTING GROUP

Compound	*Procedure*[a]	*Product*	*Yield (%)*
6	*A*	1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride	83
7α	*A*[b]	Methyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride	64
	B	Methyl 2-amino-2-deoxy-α-D-glucopyranoside	52[c]
	C	Methyl 2-amino-2-deoxy-α-D-glucopyranoside	72.5
9	*B*	Ethyl 2-amino-2-deoxy-α-D-glucopyranoside	99; 62[c]
18	*A*[b]	Methyl 2-amino-2-deoxy-α-D-glucofuranoside hydrochloride	68
	C	Methyl 2-amino-2-deoxy-α-D-glucofuranoside	65.5
19	*A*	Methyl 3,5,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucofuranoside hydrochloride	59

[a]See Experimental. [b]In aqueous solution. [c]Yield of the crystalline *N*-benzyloxycarbonyl derivative, based on the starting compound.

7α. Procedure *C* was similar to that used[15] to remove the *N*-(2,4-dinitrophenyl) group in similar aminoglycosides, and involved basic hydrolysis of the *N*-acylvinyl derivative in aqueous acetone solution in the presence of Amberlite IRA-400 (HO^-) resin. The aminoglycoside was the only product and was subsequently isolated in good yield.

Methyl 2-amino-2-deoxy-α-D-glucofuranoside[12] was obtained as a syrup, but the hydrochloride was crystalline, as was the hydrochloride of its triacetate. Methyl and ethyl 2-amino-2-deoxy-α-D-glucopyranoside and/or their hydrochlorides had properties similar to those described[16–19], and were further characterised as their *N*-benzyloxycarbonyl derivatives[16,17,20].

The above results indicate that the 2,2-dialkoxycarbonylvinyl group can be compared favourably, in many respects, with conventional protecting groups. It is as easily introduced and leads to better yields of α,β-glycopyranosides than, for example, the acetyl group in the alkyl glycosidations catalysed by hydrogen chloride (*cf.* ref. 13). In glycosidations in the presence of a cation-exchange resin, 87% yields of α,β-mixtures of glyco-pyranosides and -furanosides were produced (*cf.* 91% of α,β-glycopyranosides using the acetyl group[21]), but the higher complexity of the reaction was compensated by the fact that 25% of the furanoside **18** could be isolated easily. The route is much more convenient than those using the *N*-(2,4-dinitrophenyl) derivative of 2-amino-2-deoxy-D-glucose[15] or the free amino sugar[12,19b]. The acylvinyl groups can be easily removed under mild conditions which do not affect the glycosidic linkage.

EXPERIMENTAL

General methods. — Solutions were dried with $MgSO_4$ and concentrated under diminished pressure at <50°. Melting points were determined with a Büchi apparatus and are uncorrected. Elemental analyses were conducted at the Instituto de Química Orgánica General, C.S.I.C., Madrid. Optical rotations were measured with a Perkin–Elmer 241Mc polarimeter. U.v. spectra were recorded with a Beckman DB-GT spectrophotometer, and i.r. spectra with a Perkin–Elmer 299 and 599B spectrophotometer. Raman spectra were measured for powdered samples using a Ramanor U-1000 (5145 Å) spectrophotometer. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si), unless otherwise stated, using Perkin–Elmer R-12B (60 MHz), R-32 (90 MHz), and Bruker WM-360 (360 MHz) spectrometers. Assignments were confirmed by decoupling experiments. T.l.c. was performed on Silica Gel $60F_{254}$ (Merck) with detection by charring with sulphuric acid or by u.v. light (254 nm). Silica Gel 60 (Merck) was used for column chromatography. Identification of compounds was based on mixture m.p., i.r. spectra, and chromatography. Acetates were prepared by treating a cooled solution of the polyol (1 part) in pyridine (10 parts) with acetic anhydride (5 parts); after 24 h at 0°, the mixture was poured on to ice, and the crystalline precipitate (unless otherwise stated) was recrystallised from the solvent indicated.

2-Deoxy-[(2,2-dimethoxycarbonylvinyl)amino]-α-D-glucopyranose (**1**). — *Procedure* A. To a stirred solution of 2-amino-2-deoxy-D-glucose hydrochloride (2.16 g, 10 mmol) and sodium carbonate (0.53 g, 5 mmol) in water (8 mL) was added methyl 3-methoxy-2-methoxycarbonylacrylate[22] (3.48 g, 20 mmol). The product (3.31 g, 98%) crystallised rapidly and, after recrystallisation from ethanol, had m.p. 164–165°, $[\alpha]_{5461}^{16}$ +132° (*c* 1, methanol). Spectral data are listed in Tables I and II.

Anal. Calc. for $C_{12}H_{19}NO_9$: C, 44.86; H, 5.96; N, 4.35. Found: C, 44.50; H, 6.04; N, 4.18.

Procedure B. A mixture of 2-amino-2-deoxy-D-glucose hydrochloride (4.32 g, 20 mmol), methyl 3-methoxy-2-methoxycarbonylacrylate (3.48 g, 20 mmol), triethylamine (7 mL), and ethanol (110 mL) was heated under reflux for 0.5 h, concentrated until initial crystallisation, and refrigerated overnight. The product (5.71 g, 89%) was collected and recrystallised from ethanol to give **1**, m.p. 164–165°, which was identical with the sample described above.

The tetra-acetate **2** (98%) had m.p. 120–121° (from ethanol), $[\alpha]_{5461}^{18}$ +136° (*c* 1, chloroform). Spectral data are listed in Tables I and II.

Anal. Calc. for $C_{20}H_{27}NO_{13}$: C, 49.08; H, 5.56; N, 2.86. Found: C, 49.17; H, 5.47; N, 3.00.

2-Deoxy-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (**3**). — Prepared from ethyl 3-ethoxy-2-ethoxycarbonylacrylate by procedure *A* (98%), **3**[5] had m.p. 119–120° (from ethanol), $[\alpha]_{5461}^{18}$ +118° (*c* 1, methanol).

The tetra-acetate[5] **4** (78%) had m.p. 101–102° (from ethanol–water), $[\alpha]_{5461}^{20}$ +138° (*c* 1, chloroform). The spectral data for **3** and **4** are listed in Tables I and II.

2-Deoxy-2-[(2,2-diacetylvinyl)amino]-α-D-glucopyranose (**5**). — Prepared from 3-acetyl-4-ethoxy-3-buten-2-one[23] by procedures *A* (98%) and *B* (83%), **5** had m.p. 204–205° (from ethanol), $[\alpha]_{5461}^{22}$ +189° (*c* 1, methanol).

Anal. Calc. for $C_{12}H_{19}NO_7$: C, 49.82; H, 6.62; N, 4.84. Found: C, 49.56; H, 6.92; N, 4.91.

The tetra-acetate **6** (78%) had m.p. 137–138° (from ethanol), $[\alpha]_{5461}^{20}$ +135° (*c* 1, chloroform). The spectral data of **5** and **6** are listed in Tables I and II.

Anal. Calc. for $C_{20}H_{27}NO_{11}$: C, 52.51; H, 5.95; N, 3.06. Found: C, 52.56; H, 6.24; N, 3.18.

Methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**7α**). — Prepared from methyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride[20] and methyl 3-methoxy-2-methoxycarbonylacrylate by procedure *B* (94%), **7α** had m.p. 158–159° (from ethanol), $[\alpha]_{5461}^{27}$ +142° (*c* 1, ethanol).

Anal. Calc. for $C_{13}H_{21}NO_9 \cdot H_2O$: C, 44.19; H, 6.51; N, 3.97. Found: C, 44.59; H, 6.25; N, 3.86.

In an analytical oxidation[24], **7α** consumed 1.01 mol of sodium metaperiodate (calc. , 1.0 mol), and no formaldehyde or formic acid was liberated.

The corresponding tri-acetate **8α** (72%) had m.p. 96–98° (from ethanol),

$[\alpha]_{5461}^{28}$ +200° (*c* 1, ethanol). The spectral data for **7α** and **8α** are listed in Tables I and II.

Anal. Calc. for $C_{19}H_{27}NO_{12}$: C, 49.45; H, 5.89; N, 3.03. Found: C, 49.23; H, 5.89; N, 3.07.

Methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]-β-D-glucopyranoside (**7β**). — Prepared from methyl 2-amino-2-deoxy-β-D-glucopyranoside hydrochloride[17] and methyl 3-methoxy-2-methoxycarbonylacrylate by procedure *A* (97%), **7β** had m.p. 173–175° (from ethanol), $[\alpha]_{5461}^{21}$ −10° (*c* 1, ethanol).

Anal. Calc. for $C_{13}H_{21}NO_9$: C, 46.56; H, 6.31; N, 4.17. Found: C, 46.30; H, 6.50; N, 4.29.

The corresponding tri-acetate **8β** (83%) had m.p. 110–112° (from ethanol), $[\alpha]_{5461}^{22}$ +45° (*c* 1, chloroform). The spectral data of **7β** and **8β** are listed in Tables I and II.

Anal. Calc. for $C_{19}H_{27}NO_{12}$: C, 49.45; H, 5.89; N, 3.03. Found: C, 49.55; H, 6.08; N, 3.20.

Ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**9**). — Prepared from ethyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride[18] and ethyl 3-ethoxy-2-ethoxycarbonylacrylate by procedures *A* (98%) and *B* (55%), **9** had m.p. 115–116° (from ethanol), $[\alpha]_{5461}^{27}$ +144° (*c* 1, ethanol).

Anal. Calc. for $C_{16}H_{27}NO_9$: C, 50.92; H, 7.21; N, 3.71. Found: C, 50.53; H, 7.28; N, 3.97.

The tri-acetate **10** (78%) had m.p. 97–98° (from ethanol), $[\alpha]_{5461}^{26}$ +174° (*c* 1, ethanol). The spectral data for **9** and **10** are listed in Tables I and II.

Anal. Calc. for $C_{22}H_{23}NO_{12}$: C, 52.47; H, 6.60; N, 2.78. Found: C, 52.43; H, 6.68; N, 3.05.

Methyl 2-[(Z)-(2-benzoylvinyl)amino]-2-deoxy-α-D-glucopyranoside (**14**). — A mixture of methyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride (1.48 g, 10 mmol), benzoylacetaldehyde[25] (1.48 g, 10 mmol), triethylamine (1 mL), and methanol (50 mL) was heated under reflux for 0.5 h and then concentrated. Crystallisation of the residue from ethanol (20 mL) afforded a crystalline mixture (2.16 g) of **14** (R_F 0.54; chloroform–ethanol, 5:1) and minor amounts of a product of R_F 0.33. Column chromatography afforded **14** (1.35 g, 40%), m.p. 176–177°, $[\alpha]_{5461}^{27}$ +272° (*c* 1, ethanol); λ_{max}^{EtOH} 243 and 343 nm (log ε 3.95 and 4.27); ν_{max}^{KBr} 3470m, 3350m, 3200sh (OH, NH), 1630vs (C=O), 1585m (ring, C=C–NH), and 1530 cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (60 MHz, Me_2SO-d_6): δ 10.23 (dd, 1 H, exchangeable with D_2O, $J_{NH,1'}$ 13.6, $J_{NH,2}$ 8.5 Hz, NH), 7.80 (m, 2 H, aromatic protons), 7.45 (m, 3 H, aromatic protons), 7.15 (dd, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 5.75 (d, 1 H, H-2′), 4.68 (d, 1 H, $J_{1,2}$ 3.6, H-1), and 3.30 (s, 3 H, OMe).

Anal. Calc. for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.54; N, 4.33. Found: C, 59.03; H, 6.26; N, 4.23.

The tri-acetate **15** (87%) had m.p. 154–156° (from ethanol), $[\alpha]_{5461}^{27}$ +332° (*c* 1, chloroform); λ_{max}^{EtOH} 250 and 333 nm (log ε 3.88 and 4.26); ν_{max}^{KBr} 1745vs (AcO), 1630vs (C=O), 1585s (ring, C=C–NH), and 1550 cm^{-1} (C=C–NH). ^{1}H-N.m.r.

data (60 MHz): δ 10.05 (bdd, 1 H, exchangeable with D_2O, $J_{NH,1'}$ 13.0, $J_{NH,2}$ 8.5 Hz, NH), 7.80 (m, 2 H, aromatic protons), 7.45 (m, 3 H, aromatic protons), 6.80 (dd, 1 H, $J_{1',2'}$ 7.6 Hz, H-1'), 5.76 (d, 1 H, H-2'), 5.35 (t, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 4.95 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 4.70 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 3.95–4.45 (m, 3 H, H-5,6,6), 3.41 (s, 3 H, OMe), 3.38 (sextet, 1 H, H-2), 2.05, 1.96, and 1.93 (3 s, each 3 H, 3 Ac).

Anal. Calc. for $C_{22}H_{27}NO_9$: C, 58.79; H, 6.05; N, 3.11. Found: C, 58.40; H, 5.90; N, 3.37.

*Methyl 2-[(Z)-(2-benzoyl-1-methylvinyl)amino]-2-deoxy-α-*D*-glucopyranoside* (**16**). — Prepared from 1-phenyl-1,3-butanedione, **16** (49%) had m.p. 236–237° (from ethanol), $[\alpha]_{5461}^{29}$ +204° (*c* 1, ethanol); λ_{max}^{EtOH} 241 and 340 nm (log ε 3.90 and 4.05); ν_{max}^{KBr} 3420s, 3230w (OH, NH), 1640sh and 1590s (C=O), 1575 (ring, C=C–NH), and 1530 cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (90 MHz, Me_2SO-d_6): δ 11.26 (d, 1 H, exchangeable with D_2O, $J_{NH,2}$ 10.0 Hz, NH), 7.76 (m, 2 H, aromatic protons), 7.36 (m, 3 H, aromatic protons), 5.65 (s, 1 H, H-2'), 4.66 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 3.30 (s, 3 H, OMe), and 2.06 (s, 3 H, Me-1').

Anal. Calc. for $C_{13}H_{23}NO_6$: C, 60.49; H, 6.87; N, 4.14. Found: C, 60.31; H, 6.85; N, 3.98.

The tri-acetate **17** (86%) had m.p. 141–142° (from ethanol), $[\alpha]_{5461}^{29}$ +384° (*c* 0.5, ethanol); λ_{max}^{EtOH} 240 and 337 nm (log ε 3.90 and 4.30); ν_{max}^{KBr} 1730vs (AcO), 1605vs (C=O), 1580 and 1570s (ring, C=C–NH), and 1550s cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (90 MHz): δ 11.13 (d, 1 H, exchangeable with D_2O, $J_{NH,2}$ 10.0 Hz, NH), 7.9 (m, 2 H, aromatic protons), 7.25 (m, 3 H, aromatic protons), 5.62 (s, 1 H, H-2'), 5.34 (t, 1 H, $J_{2,3} = J_{3,4} = 10.0$ Hz, H-3), 4.90 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.77 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 3.95–4.4 (m, 3 H, H-5,6,6), 3.79 (sextet, 1 H, H-2), 3.48 (s, 3 H, OMe), 2.06 (s, 6 H, Me-1' and OAc), 1.96 (s, 3 H, OAc), and 1.90 (s, 3 H, OAc).

Anal. Calc. for $C_{23}H_{29}NO_9$: C, 59.60; H, 6.30; N, 3.02. Found: C, 59.30; H, 6.48; N, 3.15.

Glycosidation of **1**. — (*a*) A solution of **1** (1.0 g, 3.1 mmol) in methanol (50 mL) containing 2.5% of HCl was boiled under reflux for 5 h. T.l.c. (chloroform–methanol 9:1) then indicated **1** to be absent, and the presence of **7α** (R_F 0.35, major product), **7β** (R_F 0.30), and **18** (R_F 0.50; traces). The solution was stirred with lead carbonate (5.0 g), filtered, and concentrated to yield a product (1.1 g, 97%), m.p. 147–151°, $[\alpha]_{5461}^{20}$ +111° (*c* 1, ethanol). ^{1}H-N.m.r. data (60 MHz; Me_2SO- d_6 + D_2O): δ 8.05 (s, ~0.8 H, H-1' of **7α**), 7.91 (s, ~0.2 H, H-1' of **7β**), 4.80 (d, 0.72 H, $J_{1,2}$ 2.5 Hz, H-1 of **7α**), 4.50 (d, ~0.2 H, $J_{1,2}$ 8.0 Hz, H-1 of **7β**), 3.84 (bs, 3 H, CO_2Me), 3.71 (bs, 3 H, CO_2Me), 3.55 (s, OMe of **7β**), and 3.48 (s, OMe of **7α**). Several recrystallisations from ethanol afforded **7α** (0.57 g, 55%), m.p. 158–159°.

Acetylation of a sample (0.5 g) of the crude glycoside afforded a syrupy mixture (0.60 g, 87%) of **8α** (R_F 0.39; ether–hexane, 8:1) and **8β** (R_F 0.32). Column

chromatography (ether–hexane 8:1) yielded **8α** (0.36 g, 61%), m.p. 95–98°, and **8β** (0.145 g, 25%), m.p. 108–112°.

When a solution of **1** (1.0 g) in methanol (100 mL) containing 2.5% of HCl was left at room temperature for 140 h, no reaction occurred (t.l.c.).

(*b*) A stirred solution of **1** (2.0 g, 6.2 mmol) in methanol (100 mL) was boiled for 24 h under reflux with Amberlyst-15 (H^+) resin (16 g). The resin was collected and rinsed well with methanol, and the combined filtrate and washings were concentrated to yield a crystalline mixture (1.85 g) of **18** (R_F 0.50; t.l.c., chloroform–ethanol, 9:1), **7α** (R_F 0.35), **7β** (R_F 0.29), and **1** (R_F 0.01). Column chromatography (chloroform and then chloroform–ethanol, 9:1) afforded, first, methyl 2-deoxy-2-[(2,2-dimethoxycarbonylvinyl)amino]-α-D-glucofuranoside (**18**; 0.45 g, 21%), m.p. 145–146° (from ethanol), $[\alpha]_{5461}^{22}$ +170° (*c* 0.5, chloroform); λ_{max}^{EtOH} 284 nm (log ε 4.32); $\nu_{max}^{Me_2SO}$ 3290s (OH, NH), 1709s and 1689s (free CO_2Me in two conformations), 1662vs and 1650sh (intramolecularly bonded CO_2Me), and 1609 cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (60 MHz, Me_2SO-d_6): δ 9.30 (dd, 1 H, exchangeable with D_2O, $J_{NH,1'}$ 14.0, $J_{NH,2}$ 8.7 Hz, NH), 8.06 (d, 1 H, H-1'), 4.05 (d, 1 H, $J_{1,2}$ 4.70 Hz, H-1), 3.61 (s, 3 H, CO_2Me), 3.57 (s, 3 H, CO_2Me), and 3.30 (s, 3 H, OMe).

Anal. Calc. for $C_{13}H_{21}NO_9$: C, 46.56; H, 6.31; N, 4.17. Found: C, 46.40; H, 6.52; N, 4.01.

Compound **18** consumed[24] 1.0 mol of metaperiodate, and liberated 0.9 mol of formaldehyde but no formic acid.

The tri-acetate **19** (73%) had m.p. 105–107° (from ethanol), $[\alpha]_{5461}^{22}$ +204° (*c* 1, chloroform); λ_{max}^{EtOH} 280 nm (log ε 4.16); $\nu_{max}^{CCl_4}$ 3280vw (NH), 1760vs (AcO), 1730m and 1700m (free CO_2Me in two different conformations), 1670s (intramolecularly bonded CO_2Me), and 1610s cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (360 MHz): δ 9.43 (dd, 1 H, exchangeable with D_2O, $J_{NH,1'}$ 14.2, $J_{NH,2}$ 8.2 Hz, NH), 8.1 (d, 1 H, H-1'), 5.28 (ddd, 1 H, $J_{4,5}$ 8.4, $J_{5,6}$ 2.3, $J_{5,6'}$ 5.3 Hz, H-5), 5.25 (dd, 1 H, $J_{2,3}$ 3.6, $J_{3,4}$ 5.2 Hz, H-3), 5.11 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 4.55 (dd, 1 H, $J_{6,6'}$ −12.3 Hz, H-6), 4.39 (dd, 1 H, H-4), 4.16 (dd, 1 H, H-6'), 3.93 (ddd, 1 H, H-2), 3.78 (s, 3 H, CO_2Me), 3.73 (s, 3 H, CO_2Me), 3.49 (s, 3 H, OMe), 2.10 (s, 3 H, AcO), 2.08 (s, 3 H, AcO), and 2.02 (s, 3 H, AcO).

Anal. Calc. for $C_{19}H_{27}NO_{12}$: C, 49.45; H, 5.89; N, 3.03. Found: C, 49.18; H, 6.06; N, 3.03.

Eluted second was a mixture (0.70 g, 33%) of **7α** and **7β** in the ratio ~2:3 (^{1}H-n.m.r.). Acetylation of this mixture and subsequent preparative t.l.c. (ether–hexane, 8:1) afforded **8α** (0.26 g), m.p. 96–97°, and **8β** (0.37 g), m.p. 108–110°.

Eluted third was **1** (0.30 g). The yields of isolated **18**, **7α**, and **7β**, based on reacted **1**, were 25, 11, and 15%, respectively.

When a solution of **18** (50 mg) in methanol (2.5 mL) containing 2.5% of HCl was boiled under reflux for 5 h, an equilibrium was attained (t.l.c.) in which **7α** (main component), **7β** (trace), and **18** (trace) were present.

Glycosidation of **3**. — (*a*) A solution of **3** (1.0 g, 2.9 mmol) in ethanol (50 mL) containing 2.5% of HCl was boiled under reflux for 6 h. T.l.c. (chloroform–

ethanol 9:1) then revealed **9** (R_F 0.35), minor amounts of products having R_F 0.44, 0.41, and 0.30, and **3** (R_F 0.12). Work-up of the reaction mixture, in the usual way, yielded a syrup (0.98 g), column chromatography (chloroform–methanol, 6:1) of which afforded **9** (0.71 g, 66%), m.p. 114–117°, the tri-acetate **10** (81%) of which had m.p. 96–97°.

(*b*) Compound **3** (1.0 g, 3.9 mmol) was treated with refluxing methanol (50 mL) containing 2.5% of HCl. After 8 h, the mixture was neutralised with lead carbonate, filtered, and concentrated to crystallisation. Refrigeration afforded **7α** (0.48 g, 50%), m.p. 114–147°. Recrystallisation from ethanol gave the pure product, m.p. 156–158°.

Attempted glycosidations of **5** *and* **11–13**. — Typically, a solution of **13** (1.0 g, 3.0 mmol) in methanol (50 mL) containing 2.5% of HCl was boiled under reflux for 4 h. T.l.c. (chloroform–ethanol, 4:1) then revealed the absence of **13** and **16**, and the presence of 1-phenyl-1,3-butanedione. Work-up of the reaction mixture in the usual way gave a solid (0.9 g) which was extracted with boiling ethanol to leave 2-amino-2-deoxy-D-glucose hydrochloride (0.45 g, 69%), m.p. 190–195°.

Removal of the 2,2-diacylvinyl group. Procedure A. — (*a*) Chlorine was bubbled through a solution of **6** (0.30 g) in chloroform (5 mL) until saturation. The solution was refrigerated, and the crystalline precipitate (0.21 g), which was collected and washed thoroughly with ether, was 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride[4], m.p. 184–185° (dec.).

Likewise, methyl 3,5,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucofuranoside hydrochloride (59%) was prepared from **19** and had m.p. 198–201° (dec.; from methanol–ether), $[\alpha]_{5461}^{21}$ +102° (*c* 1, ethanol).

Anal. Calc. for $C_{13}H_{22}ClNO_8 \cdot H_2O$: C, 41.77; H, 6.48; N, 3.75. Found: C, 41.32; H, 6.47; N, 3.36.

(*b*) A solution of **7α** (0.30 g) in water (5 mL) was saturated with chlorine and left at ~0° overnight. The mixture was then extracted with chloroform, and the aqueous layer was freeze-dried. The resulting, amorphous, chromatographically homogeneous product (0.13 g, 64%) had the same mobility (p.c., Whatman No. 1 paper, 1-butanol–acetic acid–water, 12:3:5) as authentic[20] methyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride. This product was benzyloxycarbonylated[15] to yield methyl 2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside[17] (73%), m.p. 155–157°.

Likewise, methyl 2-amino-2-deoxy-α-D-glucofuranoside hydrochloride (68%) was prepared from **18** and had m.p. 234–235° (dec.; from ethanol), $[\alpha]_{5461}^{22}$ +75° (*c* 1, water).

Anal. Calc. for $C_7H_{16}ClNO_5$: C, 36.61; H, 7.02; N, 6.10; Cl 15.44. Found: C, 36.21; H, 6.52; N, 6.49; Cl, 15.02.

This compound reacted with periodate to give 1.05 mol. of formaldehyde.

Procedure B. A solution of **7α** (0.22 g) in acetone (6 mL) and conc. ammonia (8 mL) was stored at room temperature for 4 days. T.l.c. (chloroform–methanol, 6:1) then revealed methyl 3-amino-2-methoxycarbonylacrylate (R_F 0.82), minor

amounts of **7α** (R_F 0.54), and methyl 2-amino-2-deoxy-α-D-glucopyranoside (R_F 0.01). The mixture was concentrated and the residue was thoroughly extracted with ether. Column chromatography (chloroform–methanol, 6:1) of the resulting syrup afforded amorphous methyl 2-amino-2-deoxy-α-D-glucopyranoside as a solid that was characterised as its *N*-benzyloxycarbonyl derivative (52% based on **7α**), m.p. 159–160°.

Concentration of the combined ether extracts gave methyl 3-amino-2-methoxycarbonylacrylate[6b] (76 mg, 80%), m.p. 124–126° (from ethanol).

Likewise, ethyl 2-amino-2-deoxy-α-D-glucopyranoside (99%) was prepared from **9**, as a syrup, which was characterised as its *N*-benzyloxycarbonyl derivative[17] (62%), m.p. 129–131° (from ethanol).

Procedure C. — A solution of **7α** (0.15 g) in acetone–water (2:1, 10 mL) was stirred for 3 h at 40° with Amberlite IRA-400 (HO^-) resin (7.0 g). The resin was collected and rinsed well with acetone–water (2:1), and the combined filtrate and washings were concentrated at room temperature to remove the acetone, and then freeze-dried to give a product (63 mg, 72.5%) which, after storage over P_2O_5, had m.p. 148–151°. Recrystallisation from ethanol afforded methyl 2-amino-2-deoxy-α-D-glucopyranoside, m.p. 154–156°, $[\alpha]_D^{22}$ +161° (*c* 1, water); lit.[19], m.p. 155–157°, $[\alpha]_D^{22}$ +158.5° (*c* 1, water). The *N*-benzyloxycarbonyl derivative (69%) had m.p. 155–157°.

Likewise, methyl 2-amino-2-deoxy-α-D-glucofuranoside, prepared (65.5%) from **18**, was a syrup, $[\alpha]_D^{20}$ +105°, $[\alpha]_{3650}^{20}$ +300° (*c* 1, water); R_{GlcN} 2.25 (p.c., 1-butanol–acetic acid–water, 4:1:1; Whatman No. 3 paper; detection with ninhydrin or alkaline silver nitrate[26]), R_{GlcN} 1.36 and R_F 0.39 (1-butanol–pyridine–acetic acid–water, 60:45:4:30); lit.[12], $[\alpha]_D^{20}$ +105° and $[\alpha]_{3650}^{20}$ +303° (*c* 1, water), R_{GlcN} 2.23 (p.c., 1-butanol–acetic acid–water, 4:1:1), R_{GlcN} 1.38 (1-butanol–pyridine–acetic acid–water, 60:45:4:30).

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