BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1525—1528 (1973)

Aminosugars. XXI. Conformation of Cyclic Imido Groups Attached to the Glucopyranose-ring[1]

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(Received December 18, 1972)

Conformation of cyclic imido groups at different positions on *O*-acetylated-D-glucopyranose-ring was examined from the anisotropic effect of the carbonyls on vicinal ring-protons. The imide-plane at β-C_1, C_3 were deduced to be slightly inclined counter-clockwise, from the right angle to the mean plane of the pyranose ring, and that at α-C_2 and C_4 clockwise. 3-Deoxy-1,2 ; 5,6-di-*O*-isopropylidene-3-phthalimido-α-D-gluco- and -allofuranose were also examined.

Conformations of lactol-rings of monosaccharides[2] and their derivatives[3] in solution have been widely analyzed by NMR, however, those of substituents have been scarcely studied. In the course of synthetic studies of this series, we have noticed in NMR spectra of some phthalimido and succinimido derivatives that some vicinal ring protons showed a remarkable shift to lower fields, reflecting the steric direction of the magnetic anisotropy of the imide-carbonyl groups. This paper deals with the conformation of the cyclic imide-ring attached to various positions of the D-glucopyranose-ring in terms of comparison of the chemical shift of ring protons with that of the corresponding acetamido derivative.

Results and Discussion

Acetylated 2-deoxy-2-phthalimido-α- (**1**)[4,5] and -β-D-glucopyranose (**2**)[6], and 2-deoxy-2-succinimido-α- (**3**)[7] and -β-D-glucopyranose (**4**)[7,8] have been generally synthesized by the imidation method of tetra-*O*-acetyl-2-amino-2-deoxy-α- and -β-D-glucose[4,6,7,8] or by simulutaneous acetylation and imidation of mono-*N*-acylated derivative.[5] Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-α-D-glucopyranoside (**5**) and ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranoside (**6**), 1-*N*-phthalyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosylamine (**7**), methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-phthalimido-α-D-glucopyranose (**8**), and methyl 2,3,6-tri-*O*-acetyl-4-deoxy-4-phthalimido-β-D-glucopyranoside (**9**) were newly prepared by the latter method from suitable starting materials. 3-Deoxy-1,2;5,6-di-*O*-isopropylidene-3-phthalimido-α-D-allofuranose (**10**) and -α-D-glucofuranose (**11**) were synthesized by the former method from the corresponding aminosugars.

All NMR spectra of new compounds and other cyclic imide derivatives, except that of **1**[5], were measured at 100 MHz, and analyzed with double resonance techniques. To estimate the deshielding effect of imide-carbonyl groups, NMR spectra of the corres-

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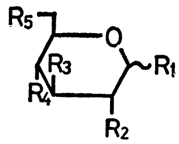
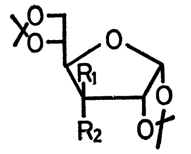


	R_1	R_2	R_3	R_4	R_5
1:	α-OAc	–N=Phth	OAc	OAc	OAc
2:	β-OAc	–N=Phth	OAc	OAc	OAc
3:	α-OAc	–N=Suc	OAc	OAc	OAc
4:	β-OAc	–N=Suc	OAc	OAc	OAc
5:	α-OAc	$-N(Ac)_2$	OAc	OAc	OAc
6:	β-OAc	$-N(Ac)_2$	OAc	OAc	OAc
7:	α-OBzl	–N=Phth	OAc	OAc	OAc
8:	α-OEt	–N=Phth	OAc	4,6-*O*–Ben	
9:	β-N=Phth	OAc	OAc	4,6-*O*–Ben	
10:	α-OMe	OAc	–N=Phth	4,6-*O*–Ben	
13:	β-OMe	OAc	OAc	–N=Phth	OAc



	R_1	R_2
11:	H	–N=Phth
12:	–N=Phth	H

Phth: Phthalyl, Suc: Succinyl, Ben: Benzylidene

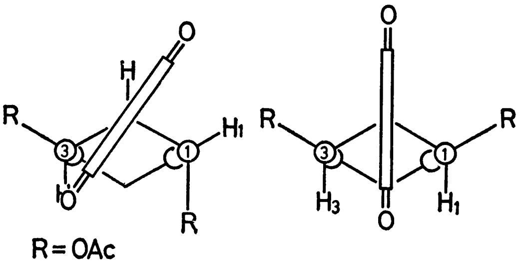
Table 1. Δδ value of ring protons between the cyclic imido and acetamido derivative of D-glucopyranoses

Compounds		Δδ value			
No.	Substituents	H_1	H_2	H_3	H_1+H_3
1	2-Phthalimido-α	−0.09	−0.27	−1.36	−1.45
2	2-Phthalimido-β	−0.74	−0.04	−0.70	−1.44
3	2-Succinimido-α	+0.07	−0.05	−1.24	−1.17
4	2-Succinimido-β	−0.67	+0.16	−0.53	−1.20
5	Benzyl 2-phthalimido-α	−0.03	−0.16	−1.42	−1.45
6	Ethyl 4,6-*O*-Ben-2-phthalimido-α	−0.08	−0.22	−1.35	−1.43
7	1-Phthalimido-β	−0.17	−0.86		
12	2-Acetylacetamido-α	−0.05	−0.20	−0.91	−0.96
13	2-Acetylacetamido-β	−0.83	−0.54	−0.72	−1.55
		H_2	H_3	H_4	H_2+H_4
8	Methyl 4,6-*O*-Ben-3-phthalimido-α	−0.53			
10	1,2; 5,6-Di-*O*-Ip-3-phthalimodo-α-D-allofura.	−0.10	−0.23	*ca.* −1.3	*ca.* −1.4
11	1,2; 5,6-Di-*O*-Ip-3-phthalimido-α-D-glucofura.	−0.38	−0.52	−0.22	−0.60
		H_3	H_4	H_5	H_3+H_5
9	4-Phthalimido-β	−0.64	+0.34	−0.89	−1.53

Ip: Isopropylidene Ben: Benzylidene

ponding acetamido derivatives were taken in the same conditions, except that of **1**—**4**[9] and **8**.[10] The corresponding acetamido derivatives of **6**, **7**, and **9** were newly prepared. The chemical shift differences (Δδ values) of vicinal ring protons between cyclic imido and acetamido derivatives were summarized in Table 1, together with that of 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α- (**12**) and -β-D-glucopyranose (**13**) reported by Inch *et al.*[9]

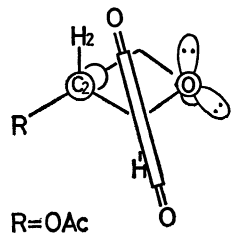
Comparison of Δδ values of **12** (α-anomer) and **13** (β-anomer) showed that only H_3 proton was shifted remarkably (0.91 ppm) in the case of **12**, while both H_1 and H_3 protons were substantially deshielded (0.83 and 0.72 ppm) in the case of **13**. The similar tendency was also observed in the case of phthalimido (**1**, **2**) and succinimido (**3**, **4**) derivatives, however, deshielding of H_3 proton in α-anomers (**1**, **3**) was further enhanced from 0.33 to 0.45 ppm compared with **12**. The steric direction of magnetic anisotropy of acetylacetamide-carbonyl groups in **12** and **13** might be, to some extent, controlled by the steric compression, and that in **1**—**4** are to be fixed by chemical bonding. Inch et al explained the difference in $\Delta\delta_{H_3}$ of **12** and **13** by the additional deshielding effect of axial C_1-acetoxy group, however, this enhancement must be attributed to the difference of the steric direction of magnetic anisotropy between non-fixed and fixed imide-carbonyl groups, in which the cyclic imide plane is inclined toward H_3 proton by the repulsion of axial C_1-acetoxy group, as was shown in Fig. 1. These deductions were supported by the fact that the deshielding effect on H_3-proton in **5** (1.42 ppm) and **6** (1.35 ppm) are still



(1) (2)

H_3 H_1 H_3 H_1
−1.0 ppm −0.02 ppm −0.18 ppm −0.18 ppm

Fig. 1. Conformation of 2-phthalimido group of **1** and **2**.



(7)

Fig. 2. Conformation of 1-phthalimido group of **7**.

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large. Difference in these values may indicate that the benzyloxy group is bulkier than the ethoxy group.

It is interesting that the sum of $\Delta\delta$ value of H_1 and H_3 protons is almost constant in 2-phthalimido derivatives (**1**, **2**, **5**, **6**), regardless of the configuration of anomeric carbon, the smaller sum in succinimido and acetylacetamido derivatives might be attributed to the absence of the anisotropy of benzene ring, and the randomness of the conformation of carbonyl groups, respectively.

On the other hand, Booth[11] showed that the plane of phthalimide in *trans*-4-(*t*-butyl)-1-phthalimidocyclohexane ring is at right angle to the mean plane of the cyclohexane ring in the preferred conformation and that the vicinal axial protons resonate at about 0.7 ppm lower magnetic field than the vicinal equatorial protons by the deshielding effect of the magnetic anisotropy of the phthalimide-carbonyl group. The difference of $\Delta\delta$ value of H_1-proton in α- and β-anomers are consistent with that of cyclohexane derivative. X-ray analysis of phthalimido-cyclohexane[12] and phthalimide itself[13] showed the co-planerity of three bonds of nitrogen and the conformation offered by Booth.[11] An attempted estimation of deshielding effect of an imide-carbonyl group on the vicinal protons from theoretically calculated values of long-range shielding[14] indicated that the values in the α-anomers and the general tendency in β-anomers consisted with that of measured. Consequently, the phthalimide-plane in **1** is inclined clockwise about 30—35°.

The $\Delta\delta$ value of H_2-proton in **7** is a little bit larger than that of H_3 in **2**, indicating an electrostatic repulsion between the carbonyl group and lone paired electrons of the lactol-oxygen (Fig. 2). In contrary, a smaller $\Delta\delta$ value of H_2 in **8** than that of H_1 and H_3 in **2** indicates a little counterclockwise inclination of the phthalimide ring, though $\Delta\delta$ value of H_4 could not be estimated. In the case of 4-phthalimido derivative (**9**), larger $\Delta\delta$ value of H_5 than that of H_3 indicates that C_5-acetoxymethyl is bulkier than C_3-acetoxy group.

In case of 3-deoxy-1,2-*O*-isopropylidene-3-phthalimido-α-D-furanoses in which C_2 and C_3 atoms are displaced in opposite side from the plane of the other ring atoms, the remarkable shift of H_5 in **10** indicates that the phthalimide ring is inclined clockwise about 30°, in order to decrease the steric hindrance with endo-methyl of 1,2-*O*-isopropylidene group and the repulsion with C_2-oxygen, while the phthalimido group in **11** seems to be free from such hindrances.

Thus, the steric direction of anisotropy of cyclic imido group is diagnostic for the steric compression and electrostatic effect of environment.

Experimental

Melting points were determined with Yanaco micro melting point apparatus and not corrected. Optical rotations were measured with a Carl Zeiss LEP-Al Polarimeter, in a 0.5-dm tube. NMR spectra were taken with JEOL 4H-100 NMR spectrometer in 10% deuteriochloroform solution containing tetramethylsilane as an internal reference. Chemical shifts and coupling constants were given in δ and Hz units, respectively.

General Synthesis of Cyclic Imido Derivatives: a) Free aminosugars were treated with phthalic anhydride or succinic anhydride in appropriate quantity of methanol, and after standing overnight the corresponding monoacylated compounds were obtained as precipitates or as a sirup by evaporation of the solution. The products were dried over phosphorous pentoxide and then treated with acetic anhydride (2 equimolar amounts) in pyridine solution. After standing 1 day at room temperature the mixture was poured into ice-water, and precipitates appeared (**6**) were filtrated and recrystallized from suitable solvents. When a sirup deposited, it was extracted with chloroform, and the sirup obtained from the extracts were purified chromatographically, using a column or preparative thin layer of silicagel (**5**, **7**, **8**, **9**).

b) A solution of aminosugar (1 mmol) and phthalic anhydride (1.1 mmol) in pyridine (1 ml) was kept overnight at room temperature, and then acetic anhydride (2 mmol) was added. After 24 hr, the mixture was poured into ice-water, the sirup deposited was extracted with chloroform and treated in the usual manner. The product was chromatographed on silica gel column (**10**, **11**).

*Benzyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-α-D-glucopyranoside (**5**)* was prepared from benzyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride.[15] A sirup was obtained in 24% yield. $[\alpha]_D^{23}=+173°$ (*c* 1.69, $CHCl_3$); NMR: 1.85, 2.03, and 2.10 (3×Ac), 3.80—4.35 (H_5, H_6, and $H_{6'}$; m), 4.45 and 4.72 (–CH_2–; ABq, $J_{AB}=11.75$), 4.52 (H_2; q, $J_{1,2}=3.75$, $J_{2,3}=11.25$), 5.00 (H_1; d), 5.08 (H_4; t, $J_{3,4}=J_{4,5}=10.0$), 6.70 (H_3; q), 7.10 (Ph; s), 7.80 (Ph; m).

Found: C, 61.20; H, 5.19; N, 2.80%. Calcd for $C_{27}H_{27}NO_{10}$: C, 61.71; H, 5.18; N, 2.67%.

*Ethyl 3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranoside (**6**)* was obtained in 26% yield from ethyl 2-acetamido-2-deoxy-α-D-glucopyranoside[16] by benzylidenation, de-*N*-acetylation, and phthalimidation. $[\alpha]_D^{23}=+125°$ (*c* 0.88, $CHCl_3$); NMR: 1.10 (CH_3; t, $J=7.0$), 1.90 (OAc), 3.2—4.4 (–CH_2–; H_4, H_5, H_6 and $H_{6'}$), 4.55 (H_2; q, $J_{1,2}=3.75$, $J_{2,3}=11.25$), 4.93 (H_1; d), 5.52 (–CH=; s), 6.70 (H_3; q, $J_{3,4}=10.0$), 7.3—7.9 (2×Ph; m).

Found: C, 64.23; H, 5.39; N, 3.00%. Calcd for $C_{25}H_{25}NO_8$: C, 64.39; H, 5.49; N, 2.92%.

The corresponding acetamide derivative was prepared by the treatment with acetic anhydride in pyridine in 54% yield. Mp. 181.5—182°C (EtOH); $[\alpha]_D^{20}=+44.6°$ (*c* 1.09, $CHCl_3$); NMR: 1.25 (CH_3; t, $J=7.0$), 1.98 (OAc), 2.08 (NAc), 3.4—4.1 (H_4, H_5, H_6, H_6, and –CH_2–), 4.33 (H_2: sextet, $J_{1,2}=3.75$, $J_{2,3}=J_{H_3,NH}=10.0$), 4.85 (H_1; d), 5.35 (H_3; t, $J_{3,4}=10.0$), 5.55 (–CH=; s), 5.90 (NH; d), 7.40 (Ph; m).

Found: C, 60.03; H, 6.62; N, 3.65%. Calcd for $C_{19}H_{25}NO_7$: C, 60.14; H, 6.64; N, 3.69%.

*1-N-Phthalimido-2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosylamine (**7**)* was prepared from 4,6-*O*-benzylidene-β-D-glucopyranosylamine[17] in 93% yield, and recrystallized from ethyl acetate. Mp. 238.5—240°C; $[\alpha]_D^{23}=-37.0°$

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(*c* 1.01, $CHCl_3$); NMR: 1.90 and 2.05 (2×OAc), 3.6—4.4 (H_4, H_5, H_6, and H_6'; m), 5.47 (H_3; t, $J_{2,3}=J_{3,4}=9.0$) 5.49 (H_1; d, $J_{1,2}=9.0$), 5.04 (–CH=; s), 6.18 (H_2; t), 7.5—7.9 (2×Ph; m).

Found: C, 61.84; H, 4.81; N, 2.86%. Calcd for $C_{25}H_{23}NO_9$: C, 62.36; H, 4.81; N, 2.86%.

The corresponding *N*-acetamido derivative was prepared in the usual manner in 91% yield. Mp. 228—229°C; $[\alpha]_D^{23}=-20.9°$ (*c* 0.99, $CHCl_3$); NMR: 1.95—2.05 (2×OAc and NAc), 3.6—4.4 (H_4, H_5, H_6, and H_6), 4.90 (H_3; t, $J_{2,3}=J_{3,4}=10.0$), 5.32 (H_1; d, and H_2; t, $J_{1,2}=J_{2,3}=J_{N,H}=10.0$), 5.45 (–CH=; s), 6.17 (NH), 7.34 (Ph; m).

Found: C, 57.39; H, 5.79; N, 3.54%. Calcd for $C_{19}H_{23}NO_8$: C, 58.01; H, 5.89; N, 3.59%.

Methyl 4,6-O-benzylidene-3-deoxy-3-phthalimido-α-D-glucopyranoside (8) was prepared from methyl 3-amino-3-deoxy-4,6-*O*-benzylidene-α-D-glucopyranoside.[10] Mp. 225—230°C; $[\alpha]_D^{23}=+8.4°$ (*c* 0.71, $CHCl_3$); NMR: 1.93 (OAc), 3.45 (OCH_3), *ca.* 3.6—4.1 (H_6 and $H_{6'}$), 4.30 (H_5; m), 4.58 (H_4; t, $J_{3,4}=J_{4,5}=10.0$), 4.90 (H_3; t, $J_{2,3}=10.0$), 5.02 (H_1; d, $J_{1,2}=3.0$), 5.48 (–CH=; s), 5.60 (H_2; q).

Found: C, 62.98; H, 5.15; N, 2.99%. Calcd for $C_{24}H_{23}NO_8$: C, 63.57; H, 5.11; N, 3.09%.

Methyl 2,3,6-tri-O-acetyl-4-deoxy-4-phthalimido-β-D-glucopyranoside (9) was prepared in 30% yield from sirupy methyl 4-amino-4-deoxy-β-D-glucopyranoside, which was synthesized as follows. The crystals[18] (mp 80—90°C) obtained by glycosidation of D-galactose in methanol containing 1% of hydrogen chloride was treated as described in the literature[19] to give a sirupy product in 11% over all yield. Mp. 180—180.5°C; $[\alpha]_D^{23}=-87.1°$ (*c* 1.02, $CHCl_3$); NMR: 1.82, 1.95, 2.03 (3×OAc), 3.53 (OCH_3), 4.06 and 4.28 (H_6 and H_6'; d, ABq, $J_{6,6'}=12.5$, $J_{5,6'}=J_{5,6}=3.1$), 4.44 (H_4; t, $J_{4,5}=10.0$, $J_{3,4}=9.1$), 4.58 (H_1; d, $J_{1,2}=8.1$), 4.57 (H_5; sextet), 5.05 (H_2; q, $J_{2,3}=9.0$), 5.79 (H_3; t), 7.80 (Ph; m).

Found: C, 56.00; H, 5.24; N, 3.09%. Calcd for $C_{21}H_{23}NO_{10}$: C, 56.12; H, 5.16; N, 3.12%.

The corresponding acetamido derivative was prepared in the usual manner in 48% yield. Mp. 200—200.5°C; $[\alpha]_D^{23}=+13.8°$ (*c* 1.0, $CHCl_3$); NMR: 1.90, 2.02, 2.07 (3×OAc and NAc), 3.48 (OCH_3), 3.68 (H_5; sextet, $J_{5,6}=J_{5,6'}=3.75$, $J_{4,5}=9.5$), 4.10 (H_4; t, $J_{3,4}=9.5$), 4.23 (H_6 and $H_{6'}$; d), 4.42 (H_1; d, $J_{1,2}=7.5$), 4.95 (H_2; q, $J_{2,3}=9.5$), 5.15 (H_3; t).

Found: C, 49.87; H, 6.35; N, 3.95%. Calcd for $C_{15}H_{23}NO_9$: C, 49.86; H, 6.42; N, 3.88%.

3-Deoxy-3-phthalimido-1,2;5,6-di-O-isopropylidene-α-D-allofuranose (10) was prepared from 3-amino-3-deoxy-1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose[20] in 67% yield. Recrystallization from ethanol gave a bulk solid. Mp. 131—132°C; $[\alpha]_D^{23}=+159°$ (*c* 1.04, $CHCl_3$); NMR: 1.28 and 1.60 (4×CH_3), *ca.* 3.8—4.3 (H_5, H_6, and $H_{6'}$; m), 4.48 (H_3; q, $J_{3,4}=10.0$, $J_{2,3}=5.0$), 4.73 (H_2; t, $J_{1,2}=4.5$), 5.52 (H_4; q, $J_{4,5}=5.0$), 5.88 (H_1; d), 7.25 (Ph; m).

Found: C, 61.81; H, 5.91; N, 3.56%. Calcd for $C_{20}H_{23}NO_7$: C, 61.69; H, 5.95; N, 3.60%.

3-Deoxy-3-phthalimido-1,2;5,6-di-O-isopropylidene-α-D-glucofuranose (11) was prepared from 3-amino-3-deoxy-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose[21] in 86% yield. $[\alpha]_D^{23}=+32.7°$ (*c* 1.09, $CHCl_3$); NMR: 1.08, 1.33, 1.55 (4×CH_3), 3.7—4.0 (H_5, H_6, and $H_{6'}$), 4.42 (H_4; q, $J_{3,4}=5.25$, $J_{4,5}=7.50$), 4.92 (H_3; d), 4.95 (H_2; d, $J_{1,2}=3.75$), 6.31 (H_1; d), 7.82 (Ph; m).

Found: C, 62.13; H, 6.15; N, 3.56%. Calcd for $C_{20}H_{23}NO_7$: C, 61.69; H, 5.95; N, 3.60%.

NMR Data of Known Compounds. 1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**2**)[6,8]; 1.38, 1.99, 2.04, 2.11 (4×OAc), *ca.* 3.9—4.45 (H_5, H_6, and $H_{6'}$), 4.48 (H_2; q, $J_{1,2}=8.75$, $J_{2,3}=10.5$), 5.21 (H_4; t, $J_{3,4}=J_{4,5}=9.5$), 5.90 (H_3; q), 6.51 (H_1; d), 7.81 (Ph; m).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-succinimido-α-D-glucopyranoside (**3**)[7]; 1.95; 2.02, 2.04, and 2.08 (4×OAc), 2.64 ($-CH_2CH_2-$; s), *ca.* 3.8—4.4 (H_5, H_6 and H_6), 4.51 (H_2; q, $J_{1,2}=3.75$, $J_{2,3}=11.25$), 5.07 (H_4; t, $J_{3,4}=J_{4,5}=9.5$), 6.13 (H_1; d), 6.44 (H_3; q).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-succinimido-β-D-glucopyranoside (**4**)[7]; 1.93, 2.00, 2.02, and 2.06 (4×OAc), 2.63 ($-CH_2CH_2-$; s), 3.94 (H_5; m), *ca.* 4.0—4.4 (H_6 and H_6), 4.28 (H_2; t), 5.13 (H_4; t, $J_{3,4}=J_{4,5}=9.0$), 5.73 (H_3; t, $J_{2,3}=10.0$), 6.44 (H_1; d).

Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (**5**)[22]; (–NH proton was diminished by shaking with deuterium oxide), 1.92, 2.05, 2.13 (3×OAc, NAc), 3.8—4.25 (H_5, H_6, and $H_{6'}$), 4.36 (H_2; q, $J_{1,2}=3.75$, $J_{2,3}=7.5$), 4.51 and 4.72 ($-CH_2-$; ABq, $J_{AB}=11.5$), 4.97 (H_1; d), 5.13 (H_4; t, $J_{3,4}=J_{4,5}=9.5$), 5.28 (H_3; q), 7.48 (Ph).

3-Acetamido-3-deoxy-1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose (**10**)[23]; 1.35, 1.45, 1.58 (4×CH_3), 2.02 (NAc), 3.8—4.32 (H_4, H_5, H_6, and $H_{6'}$). (H_3 was assigned to 4.25 by irradiating at H_2) *ca.* 4.2 (H_4), 4.62 (H_2; q, $J_{1,2}=3.75$, $J_{2,3}=4.75$), 5.84 (H_1; d), 6.07 (NH; d, $J=8.0$).

3-Acetamido-3-deoxy-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (**11**)[24]; 1.29, 1.34, 1.42, 1.50 (4×CH_3), 2.00 (NAc), 3.86 (H_6; q, $J_{6,6'}=8.50$), 4.10 ($H_{6'}$; q, $J_{4,5}=J_{5,6}=J_{5,6'}=6.25$), 4.20 ($H_4$; q, $J_{3,4}=3.50$), 4.31 (H_5; q), 4.40 (H_3; q, $J_{H_3\text{-}NH}=7.0$), 4.57 (H_2; d, $J_{1,2}=3.75$), 5.85 (H_1; d), 6.78 (NH; d).

The authors are indebted to Mr. K. Fukukawa and H. Matsumoto for NMR measurements, Mr. Y. Ogura for his help for a part of experiments, and members of Laboratory of Organic Analysis for microelemental analysis.

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