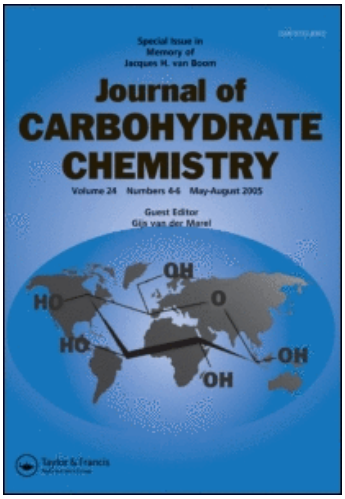

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

^{1}H NMR Analyses of Rotameric Distribution of C5-C6 bonds of D-Glucopyranoses in Solution

Yoshihiro Nishida[a]; Hiroshi Hori[a]; Hiroshi Ohrui[a]; Hiroshi Meguro[a]
[a] Department of Food Chemistry, Tohoku University, Sendai, Jpn

To cite this Article Nishida, Yoshihiro , Hori, Hiroshi , Ohrui, Hiroshi and Meguro, Hiroshi(1988) '^{1}H NMR Analyses of Rotameric Distribution of C5-C6 bonds of D-Glucopyranoses in Solution', Journal of Carbohydrate Chemistry, 7: 1, 239 — 250
To link to this Article: DOI: 10.1080/07328308808058917
URL: http://dx.doi.org/10.1080/07328308808058917

J. CARBOHYDRATE CHEMISTRY, 7(1), 239-250 (1988)

^{1}H NMR ANALYSES OF ROTAMERIC DISTRIBUTION OF C5-C6 BONDS OF D-GLUCOPYRANOSES IN SOLUTION

Yoshihiro Nishida, Hiroshi Hori, Hiroshi Ohrui*
and Hiroshi Meguro

Department of Food Chemistry
Tohoku University, Tsutsumi-
dori-Amamiya 1-1, Sendai, Jpn

Received November 20, 1987 - Final Form January 26, 1988

ABSTRACTS

^{1}H NMR signals of H-6proR and H-6proS protons of D-glucoses and their per-O-acylated (acetyl and benzoyl) derivatives were unambiguously assigned by chiral deuteration at the C-6 position. The $J_{H5,H\text{-}6proR}$ and $J_{H5,H\text{-}6proS}$ values thus obtained enabled us to calculate the rotameric distributions of *gg*, *gt* and *tg* conformers. For the calculations, conventional equations (*A* and *B*) and novel equations accounting for possible departure of the three conformers from perfect staggering, were employed. The results showed that D-glucoses irrespective of solvents and protecting groups were predominant in two conformers *gg* and *gt* in an approximate ratio of 60 and 40, respectively, with a negligibly low population of the *tg* conformer. These results were in complete accordance with the statistical study of X-ray data of D-glucoses.

INTRODUCTION

Exo cyclic C5-C6 bonds of D-Glucoses are expected to exist in conformational equilibrium between three staggered conformers, namely, *gg* (*gauche-gauche*), *gt* (*gauche-trans*) and *gt* (*trans-gauche*) (FIG. 1). Determination of the rotameric distribution of C5-C6 bonds has been the subject of many conformational studies of D-glucose, in which semi-empirical energy calculations,[1] X-ray diffractions,[2] chiroptical methods[3] and nuclear magnetic resonance spectroscopy[4] have been employed.

Distributions of conformers derived from energy calculations varied extensively among the reports and seemed to depend on the parameters employed. In X-ray analyses, Marchessault and Perez[2] reported statistical data of more than one hundred solid D-glucoses including their derivatives to show the distributions of *gg* : *gt* : *tg* in the ratio of 60 : 40 : 0, respectively. It is noteworthy that the *tg*-conformer was not found among these crystalline compounds. The chiroptical methods are informative for studying conformations in solution. However, reported results were in contradiction between Yamana[5] and Lemieux[6] who assigned the *tg* and *gt* conformers of D-glucose in water solution respectively using molecular rotation rules. Using circular dichroism, Nakanishi and his co-workers[7] showed the *gg*-preference of per-O-benzoylated D-glucose in dilute ethanol solution. NMR spectroscopy has provided a promising method for the study of solution conformations because the relationship between vicinal ^1H - ^1H coupling constants and the relative geometries between the two protons are well established by a Karplus rule.[8] For the present purpose, a set of $J_{H5,H\text{-}6proR}$ and $J_{H5,H\text{-}6proS}$ coupling constants can be used. Studies of this type were initiated by Lemieux[9] and Hall[10] in the 1960's but more recent results have been reported.[11] However, most of the results were based on ambiguous assignments of the two C-6 protons, and thereby are inconsistent.[9-11] Analyses based on the unequivocal designation of the two protons were reported by Gagnaire *et al.*[12] and Rao and Perlin[13] who employed selective deuteration of the H-6proR or H-6proS to show the *gg* and *gt* are predominant conformers in solution.

The purpose in this study was to calculate the rotameric distributions of *gg*, *gt* and *tg* of D-glucose in solution by ^1H NMR analysis. Here, we apply our method of chiral deuteration at the C-6 position of D-hexoses[14-17] to make unambiguous assignments of the two C-6 protons and apply conventional Karplus type equations to calculate the rotameric distributions.

RESULTS AND DISCUSSION

a) Assignments of H-6proR and H-6proS signals

Unequivocal assignment of H-6proR and H-6proS signals is a crucial problem in ^1H NMR analyses of conformations about C5-C6 bonds because

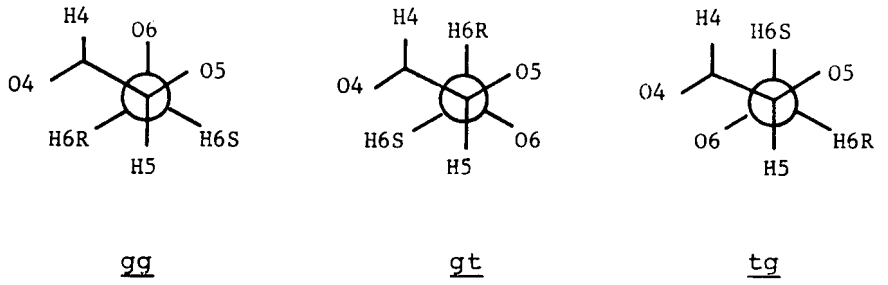

FIG. 1 Three Possible Conformers about C5-C6 Bonds of D-glucose, gg, gt and tg.

ambiguous assignments of the two protons might lead to proposing a wrong conformation. In order to circumvent this problem an assumption has often been used[18,19] that since the *tg*-conformer would be most unfavored because of a strong 1,3-*syn-periplanar* repulsion between C4-O4 and C6-O6 bonds, the proton with a larger vicinal coupling constant with H-5 is assignable to H-6proR. Validity of this assumption was not clear because in some energy calculations[1,20,21] a considerably higher *tg*-population was expected over *gg* or *gt*. In this study we employed our method of selective deuteration at the C-6 position of D-hexoses, and H-6proR and H-6proS signals of all compounds studied in this paper were unequivocally differentiated. An example is presented in FIG. 2, methyl β-D-glucopyranoside and its (6S)-(6-$^{2}H_{1}$)-analog. Since H-6proS proton is replaced by a deuterium in the latter compound, the signals that disappeared in the spectrum can be assigned to H-6proS, and the signals in which the coupling pattern is changed from a double-doublet to a doublet is assignable to H-6proR. Here, there was no detectable difference in coupling constant of H-6proR with H-5 between the non-deuterated compound and its deuterated analog (within ± 0.2 Hz), while the chemical shift of H-6proR signals showed upper-field shift by *ca.* 0.015-0.020 ppm compared with the signal of the non-deuterated compound. These phenomena were common among all of the compounds studied here.

The chemical shifts (δ ppm) and the vicinal coupling constants (J Hz) of the two C-6 protons thus obtained are summerized in Table 1. The data revealed that the vicinal coupling constants of the two

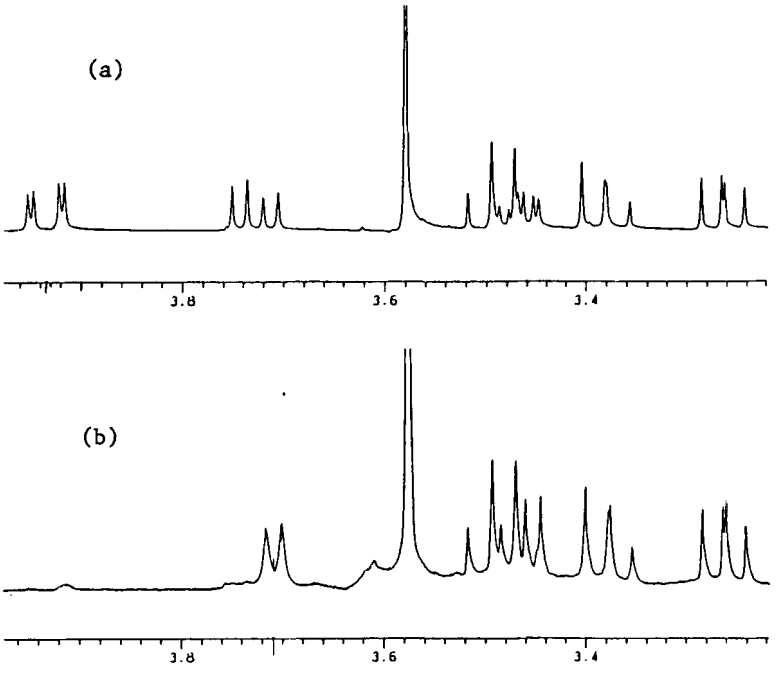

FIG. 2 400 MHz ^{1}H NMR spectra of methyl β-D-glucopyranoside in D_2O solution (a) and its (6S)-(6-$^{2}H_1$)-analog (b).

protons showed a constant relationship of $J_{H5,H\text{-}6proR} > J_{H5,H\text{-}6proS} =$ *ca.* 2 Hz among the compounds. However, the relative chemical shifts of the two protons changed completely between OH-glucose in D_2O solution (or OBz-sugars in $CDCl_3$ solution) and O-acetylated derivatives in $CDCl_3$ solution. This trend was already reported in the literature[13] and found to occure in 4,6-di-O-acetyl compounds but not in the corresponding mono-4-O-acetyl or mono-6-O-acetyl compounds.

Our assignments of H-6proR and H-6proS signals matched with those of Perkins *et al.*[19] and resulted in confirming their assumption that the proton with the larger $J_{H5,H6}$ values is assignable to H-6proR as previously mentioned.

b) Calculations of Rotameric Distributions from $J_{H5,H\text{-}6proR}$ and $J_{H5,H\text{-}6proS}$ values.

Since the interconversion among the three conformers is sufficiently fast on the NMR-time scale, $J_{H5,\ H\text{-}6proR}$ and $J_{H5,H\text{-}6proS}$ values are

TABLE 1

^{1}H NMR data [a] of two H-6 protons and rotameric distributions of D-glucoses.

Compounds	Solvents	δ(ppm) H6R	δ(ppm) H6S	J vic (Hz) H6R	J vic (Hz) H6S	Equation A gg	Equation A gt	Equation A tg	B1 gg	B1 gt	B1 tg	D gg	D gt	D tg
α-D-glucose	D_2O	3.76	3.85	5.8	1.9	56	44	0	58	56	-14	58	46	-4
β-D-glucose	D_2O	3.72	3.90	6.0	2.1	53	45	2	54	57	-11	54	48	-2
Me-α-D-glucopyranoside	D_2O	3.76	3.89	5.4	2.3	58	38	4	59	49	-8	59	41	0
	DMSO-d6	3.50	3.70	5.9	1.9	55	45	0	57	57	-14	57	47	-4
Me-β-D-glucopyranoside	D_2O	3.71	3.94	6.2	2.3	50	47	3	51	58	-9	51	49	0
penta-O-acetyl-α-D-glucopyranose	$CDCl_3$	4.28	4.08	4.3	2.1	68	28	4	71	39	-10	73	29	-2
Me-tetra-O-benzoyl α-D-glucopyranoside	$CDCl_3$	4.50	4.62	5.1	2.9	57	32	11	57	43	0	57	35	7
	$CDCl_3$/benzene-d6(1/1)	4.43	4.56	5.0	2.9	58	31	11	58	42	0	59	34	7

a. Measured at 400 MHz and 298 K using internal standard of 3-(trimethylsilyl)-propanesulfonic acid sodium salt (TPS, 0.000 ppm) for aqueous solution and tetramethysilane (TMS, 0.000 ppm) for organic solvents.

First order analysis $J_{5,6} \pm 0.2$ Hz.

observed as weighted time-averaged values reflecting the rotameric distributions. Conventionally two types of equations *A* and *B* (Table 2) have been employed in the study of D-pentofuranoses to calculate the distributions of the C4-C5 fragments.[22,23] Application of these equations to the study of D- hexoses has been restricted to the recent report of Boyd *et al.*[11] In our preliminary use of these two equations for methyl α-D-glucopyranoside, α-D-galactopyranose and their 4,6-O-benzylidene derivatives with rigid *tg* and *gg*-conformers, respectively, it was found that equation *A* and *B* showed considerable change in the distributions from each other (Table 2); the latter equation gave large minus distribution to the *tg*-conformer of D-glucose suggesting that application of equation *B* for D-hexoses should be approached cautiously. Recently Boyd *et al.*[11] reported the use of equation *B* for the conformational study of *N*-acetyl-D-glucosamines. However, they assigned the two C-6 protons incorrectly[24] on the basis that equation *B* gives large minus values when the two C-6 protons are assigned according to the assumption of Perkin *et al.*[19], and proposed the conformations *gg* : *tg* = 70 : 30 with a negligible contribution from the *gt*-conformer. In a separate paper[24] we revised their assignments and reported the conformations of *N*-acetyl-D-glucosamine in water solution to be *gg* : *gt* : *tg* = *ca.* 60 : 40 : 0 by using our chiral deuteration method and equation *A*. However the problem concerned with the unreasonable minus populations by equation *B* was not solved. These facts prompted us to check the use of equation *B* for the study on D-hexopyranoses, and in this section we wish to report that possible distortion of *gg*, *gt* and *tg* conformers from perfect staggering should be taken into account for the calculations.

The equation *B* originates in a Karplus equations (see Table 2) of Haasnoot.[25-27] This Karplus equation may be to-date one of the most sophisticated equations and widely tested in the field of carbohydrates. Its accuracy and applicability for the study on D-hexoses has been recognized.[26] Thus, the significance of this Karplus equation may depend on the accuracy of optimizing the dihedral angles of the three conformers. This can be noticed in the calculations for 4,6-O-benzylidene derivatives with rigid conformers about C5-C6 bonds. When the dihedral angles of the conformers are suitably optimized, the equations derived from the Karplus equation of Haasnoot *et al.* show the distributions of conformers in excellent accord with the *real*-conformers of the

TABLE 2

Conventional equations A and B (B1 and B2) and novel equations C - H to calculate the rotameric distributions of D-hexopyanoses.

General Formula (1)- (3)

$$As\ \underline{gg} + Bs\ \underline{gt} + Cs\ \underline{tg} = J_{H5,H6S} \quad -- (1)$$

$$A_r\ \underline{gg} + B_r\ \underline{gt} + C_r\ \underline{tg} = J_{H5,H6R} \quad -- (2)$$

$$\underline{gg} + \underline{gt} + \underline{tg} = 1 \quad -- (3)$$

Calculations

	α-D-glucose (D_2O)	α-D-galactose (D_2O)	β-D-glucose ($CDCl_3$)	β-D-galactose ($CDCl_3$)
	Methyl 2,3-di-O-acetyl-4,6-O-benzylidene			
$J_{H5,H6R}$=	5.8	7.9	5.0	1.7 (Hz)
$J_{H5,H6S}$=	1.9	4.6	11.0	1.7 (Hz)

Equations	As/Ar	Bs/Br	Cs/Cr	Dihedral angles ($\phi O5,O6$) gg	gt	tg	Rotameric Distributions (%) gg	gt	tg	gg	gt	tg	gg	gt	tg	gg	gt	tg
A	1.3/1.3	2.7/11.5	11.7/5.8	(-	-	-)	56	44	0	22	54	24	11	-5	94	94	2	4
B1[a]	2.8/0.9	3.1/10.7	10.7/5.0	-60	+60	180(°)	58	56	-14	17	63	20	-2	-2	104	100	14	-14
B2[a]	2.9/1.0	3.0/11.2	11.2/4.9	-60	+60	180	61	52	-13	20	60	20	1	2	98	102	12	-15
C	2.4/1.5	2.4/10.8	11.1/4.1	-65	+65	+175	58	48	-6				-8	10	98	103	5	-8
D	2.2/1.7	2.4/10.8	11.1/4.1	-67	+65	+175	58	46	-4				-8	10	98	104	1	-5
E	1.7/1.7[b]	2.4/10.8	11.1/4.1	-68	+65	+175	56	45	-1				-9	10	98	100	0	0
F	2.9/1.0	2.4/10.8	11.2/4.9	-60	+65	180				15	61	24	0	2	98	101	13	-14
G	3.6/0.7	2.4/10.8	11.2/4.9	-55	+65	180				15	62	23	0	2	98	103	19	-22
H	4.3/0.46	2.4/10.8	11.2/4.9	-50	+65	180				15	63	22	0	2	97	105	25	-30

a Obtained from general Karplus equations of Haasnoot et al. (ref. 24,25,26),
$J_{H,H} = 13.22\cos^2\phi - 0.99\cos\phi + \Sigma\,\Delta\chi i\{0.87 - 2.4\cos^2(\xi\phi + 19.9|\Delta\chi i|)\}$, where factors of electronegativity ($\Delta\chi i$) were set 1.3 (O-5 and O-6) and 0.4 (C-4) for equation B1 (ref. 22) and 1.22 (O-5 and O-6) and 0.08 (C-4) for equation B2 (ref. 25). Equations C - H were derived using the latter parameters.

b The values were obtained from $J_{H5,H6R}$ and $J_{H5,H6S}$ data of methyl 2,3-di-O-acetyl-4,6-benzylidene-β-D-galactopyranoside in $CDCl_3$.

benzylidine derivatives (Table 2). In the equation *B*,[23] the conformers about C5-C6 bonds are assumed to be perfectly staggered, *i.e.*, ϕO5,O6 = -60°, +60° and 180° for *gg*, *gt* and *tg*, respectively. However in a statistical study of X-ray data of more than one hundred D-glucoses and twenty D-galactoses,[2] considerable distortions from the perfect angles were presented; D-glucoses showed mean angles of *gg* and *gt* to be -66.5° and +65°, respectively, while D-galactoses showed those of *gg*, *gt* and *tg* to be -52°, +63.8° and +178.4°, respectively. These X-ray data provided useful information for optimizing the dihedral angles of three conformations in solutions.

Additional information was available from empirical force field calculations. Although the relative abundance of the three conformers varied among the reports as previously mentioned, the reported dihedral angles of the conformers with lowest energy showed overall tendencies in good accordance with the data from X-ray analysis as mentioned above. Perez *et al.*[21] showed the dihedral angles of *gg* and *gt* of acetylated D-glucoses with the lowest energy to be -70° and +60°, respectively, and Braddy[1] reported those of *gt* and *tg* to be +71.7° and +171.6°, respectively. Melberg and Rasmussen[27] documented in force field calculations of gentiobiose that the dihedral angles about the C5-C6 bonds with lowest energy are not centered symmetrically around -60°, +60° and 180°, mainly because of strong O -- O repulsion(O-6 -- O5 for *gg* and *gt* and O-6 -- O4 for *tg*), and they showed further that the distortions of the dihedral angles were in good agreement with the X-ray data.

By assuming these deviations of dihedral angles for each of the three conformers we optimized their dihedral angles in several ways using the Karplus equation of Haasnoot *et al.* to derive new equations *C-E* for D-glucoses and *F-H* for D-galactoses. These new equations were used for the rotamer calculations as shown in Table 2. First of all it is notable that the small differences in the optimized angles among *C* to *E* or *F* to *H* showed little change in the results of the calculations. The significant change was that the large minus distributions of *tg* conformers in equation *B* was considerably minimized in the *C-E* equations. This suggests that the conformers, especially *gg* and *gt* of D-glucoses in solution, might be distorted from perfect staggering in the manner predicted from X-ray studies or force field calculations. Consequently, some of the confusion in using equation *B* for the calcu-

TABLE 3

Calculations of Rotameric Distributions of D-galactopyranoses. (Ref. 30)

Compounds	Solvents	σ (ppm)		J (Hz)[b]		Populations (%)								
						Equation A			B1			G		
		H-6R	H-6S	H5,H6R	H5,H6S	*gg*	*gt*	*tg*	*gg*	*gt*	*tg*	*gg*	*gt*	*tg*
α-D-galactopyr.	D_2O	3.74	3.73	7.9	4.6	21	54	25	17	63	20	15	62	23
β-D-galactopyr.	D_2O	3.76	3.73	7.8	4.6	22	53	25	18	62	20	16	61	23
Me-α-D-galactopyr.	D_2O	3.76	3.75	8.3	4.0	21	61	18	13	70	17	15	69	16
	DMSO-d_6	3.45	3.45	6.3	6.2	27	30	43	20	38	42	21	39	40
Me-β-D-galactopyr.	D_2O	3.79	3.75	8.0	4.4	22	55	23	17	65	18	15	64	21
	DMSO-d_6	3.50	3.56	5.9	5.9	32	27	41	27	35	38	27	37	36
Penta-OAc-α-D-galactopyr.	$CDCl_3$	4.07	4.12	6.6	7.1	19	29	52	11	36	53	11	37	52
Me-tetra-OAc-β-D-galactopyr.	$CDCl_3$	4.19	4.13	6.3	7.1	21	30	49	14	33	53	14	34	51
	aceton-d_6/ $CDCl_3$ (1 : 1)	4.16	4.16	6.6	6.6	22	31	47	14	39	47	15	40	46
Me-tetra-OBz-β-D-galactopyr.	$CDCl_3$	4.69	4.45	6.3	6.6	24	29	47	17	36	47	18	37	45
	benzene-d_6 /$CDCl_3$ (1 : 1)	4.64	4.37	6.4	6.6	24	29	47	16	37	47	17	38	45

a. Measured at 400 MHz and 296 K using internal standard (0.000 ppm) of 3-(trimethylsilyl)propanesulfonic acid sodium salt for aqueous solution and tetramethylsilane for organic solution.

b. First-order analysis, $J_{5,6} \pm 0.2$ Hz.

lation of D-glucoses was eliminated. It is also noteworthy that the conventional equation *A* has parameters closer to those in the new equations *C-E* than to those in *F-H*. Since equation *A* originates from ^{1}H NMR data of a cyclic nucleoside as a rigid *gg* conformer with an angle ϕO4,O5 = *ca.* -70° (X-ray analysis)[29] and 2,3-*trans*-dimethyldioxanes (torsion angles were not defined), this equation has parameters close to those in equation *C-E* for D-glucoses. Thus, the distributions calculated by *C-E* are very similar to those calculated by equation *A* (Table 1 and 2).

In this study we calculated rotameric distributions of D-glucoses by using equations *A* and *B* in a conventional manner and a new equation *D* assuming the deviations of dihedral angles as shown in Table 2. These equations were used also for acylated derivatives without modification since small differences in the electronegativity between OH and O-acylated groups would show little change of coupling constants (order of 0.1 - 0.2 Hz).[27] The results are summarized in Table 1 together with the ^{1}H NMR data. They indicated that the rotameric distributions of D-glucoses showed a constant feature of *gg* : *gt* : *tg* = *ca.* 60-50 : 50-40 : 0, irrespective of solvents and protecting groups. That the *tg*-distribution is negligibly low is in accord with the results obtained in X-ray analysis of D-glucoses. Moreover, the relative ratio of *gg* and *gt* also showed good agreement with the X-ray data (*gg*/*gt* = 60/40). Here, the highest *gg* population was observed for penta-O-acetyl-α-D-glucopyranose (*gg* : *gt* = *ca.* 70 : 30) and the lowest population was observed in methyl β-D-glucopyranoside (*gg* : *gt* = *ca.*60: 40) and in agreement with the circular dichroism study of Nakanishi *et al.*[7,31,32]

In Table 3 are shown calculation of D-galactopyranoses by using conventional equations *A* and *B* and a new equation *G* where dihedral angles of *gg*, *gt* and *tg* were optimized to be -55°, +65° and 180°, respectively on the basis of X-ray data. The detailed discussion of conformations of D-galactoses have already been reported in our separate paper[30] using equations *A* and *B*, and the results of equation *G* are not different significantly from those of equation *B*.

ACKNOWLEDGEMENT

The authors are very grateful to Dr. J. Uzawa of RIKEN (The Institute of Physical and Chemical Research) and Mr. S. Zushi of Central

Research Institute of Meiji Seika Kaisha for their NMR measurements of a number of samples and useful discussion. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

REFERENCES AND FOOTNOTES

1. J. W. Brady, *J. Am. Chem. Soc.*, 108, 8153 (1986) and references therein.
2. R. H. Marchessault and S. Peretz, *Biopolymers*, 18, 2369 (1979).
3. C. Bertucci, P. Salvadori, G. Zullino, D. Pini and W. C. Johnson, *Carbohydrate Res.*, 149, 299 (1986).
4. A. D. Bruyn and M. Anteunis, *Carbohydrate Res.*, 47, 311 (1976).
5. S. Yamana, *Bull. Chem. Soc. Jpn.*, 30, 920 (1957).
6. R. U. Lemieux and J. C. Martin, *Carbohydrate Res.*, 13, 139 (1970).
7. J. Golok, H. W. Liu, M. Dinovi, J. Furukawa and K. Nakanishi, *Carbohydrate Res.*, 118, 135 (1983).
8. M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).
9. R. U. Lemieux and J. P. Stevens, *Can. J. Chem.*, 44, 249 (1966).
10. L. D. Hall, J. F. Manville and N. S. Bhacca, *Can. J. Chem.*, 47, 1 (1969).
11. J. Boyd, R. Porteous, N. Soffe and M. Delepierre, *Carbohydrate Res.*, 139, 35 (1985).
12. D. Gagnaire, D. Horton and F. R. Travel, *Carbohydrate Res.*, 27, 363 (1973).
13. V. S. Rao and A. S. Perlin, *Can. J. Chem.*, 61, 2688 (1983).
14. H. Ohrui, H. Horiki, H. Kishi and H. Meguro, *Agric. Biol. Chem.*, 47, 1750 (1983).
15. Y. Nishida, H. Ohrui and H. Meguro, *Tetrahedron Lett.*, 25, 1575 (1984).
16. H. Ohrui, Y. Nishida, M. Watanabe, H. Hori and H. Meguro, *Tetrahedron Lett.*, 26, 3251 (1985).
17. H. Hori, T. Nakazima, Y. Nishida, H. Ohrui and H. Meguro, *J. Carbohydrate Chem.*, 5, 585 (1986).
18. C. H. Lee and R. H. Sarma, *Biochemistry*, 15, 697 (1976).
19. S. J. Perkins, L. N. Johnson and D. C. Phillips, *Carbohydrate Res.*, 59, 19 (1977).
20. M. R. Pincus, A. W. Burgess and H. A. Scheragga, *Biopolymers*, 15, 19 (1976).
21. S. Perez and R. H. Marchessault, *Can. J. Chem.*, 56, 2866 (1978).
22. G. D. Wu, A. S. Serrianni and R. Barker, *J. Org. Chem.*, 48, 1750 (1983).

23. L. H. Koole, H. D. Boer, J. W. Haan, C. A. G. Haasnoot, P. Dael and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 362 (1986).

24. Y. Nishida, H. Hori, H. Ohrui and H. Meguro, *Carbohydrate Res.*, 170, 106 (1987).

25. C. A. G. Haasnoot, F. A. A. Leeuw and C. Altona, *Tetrahedron*, 36, 2783 (1980).

26. C. A. G. Haasnoot, F. A. A. Leeuw and C. Altona, *Bull. Soc. Chim. Berg.*, 89, 125 (1980).

27. C. Altona and C. A. G. Haasnoot, *Org. Magn. Reson.*, 13, 417 (1980).

28. S. Melberg and K. Rasmussen, *Carbohydrate Res.*, 78, 215 (1980).

29. P. C. Manor, W. Saenger, D. B. Davies, K. Jankowski and A. Rabczenko, *Biochim. Biophys. Acta*, 340, 472 (1974).

30. H. Ohrui, H. Nishida, H. Higuchi, H. Hori and H. Meguro, *Can. J. Chem.*, 65, 1145 (1987).

31. Recently,[32] Nakanishi and his co-workers reported ^{1}H NMR calculations of rotameric distributions of D-glucopyranose derivatives and compared the results with the circular dichroic data.

32. W. T. Wiesler, J. T. Vazquez and K. Nakanishi, *J. Am. Chem. Soc.*, 109, 5586 (1987).