A ^{13}C Cross Polarization–Magic Angle Spinning (CP–MAS) N.M.R. Study of Crystalline Cyclohexa-amylose Inclusion Complexes. Conformation-dependent ^{13}C Chemical Shifts are related to the Dihedral Angles of Glycosidic Linkages

Hazime Saitô,[a]* Giichi Izumi,[b] Takashi Mamizuka,[c] Sintaro Suzuki,[c] and Ryoko Tabeta[a]

[a] *Biophysics Division, National Cancer Center Research Institute, Tsukiji 5-chome, Chuo-ku, Tokyo, 104, Japan*
[b] *Institute of Microbial Chemistry, Kamiosaki, Shinagawa-ku, Tokyo, 141, Japan*
[c] *Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 167, Japan*

^{13}C Chemical shifts of the C-1 and C-4 atoms of crystalline cyclohexa-amylose enclosing a variety of guest molecules are significantly displaced as a result of host–guest interaction and are related to the dihedral angles (ϕ and ψ) at the glycosidic linkages.

We have previously shown, for several polysaccharides with a variety of glycosidic linkages, that ^{13}C chemical shifts of the C-1 and C-X atoms at the glycosidic linkages in gel[1a] and solid[1b–d] states are substantially displaced downfield (up to 5 p.p.m.) with respect to those in aqueous solution. These displacements may be interpreted by recognising a conformation-dependency of ^{13}C shifts on changes in the dihedral angles (ϕ and ψ for rotation about the C-1–O$_{gly}$ and O$_{gly}$–C-X bonds,

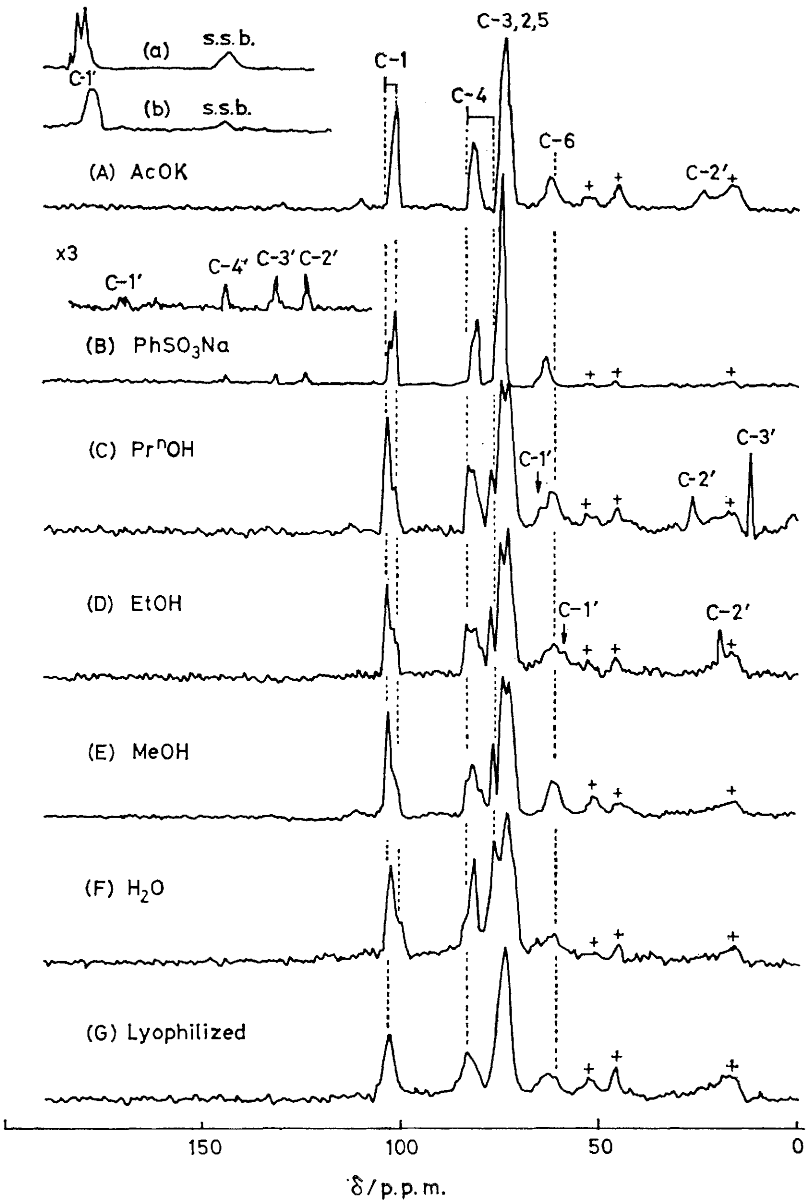

Figure 1. 75.46 MHz ^{13}C CP–MAS n.m.r. spectra of crystalline cyclohexa-amylose inclusion complexes (A—F) and of lyophilized sample (G). Contact time 1 ms; recycle time 2 s; number of transients 500—1000. Peaks marked + are from residual signals from the rotor [perdeuteriated poly(methyl methacrylate)] and probe assembly. Insets (a) and (b) are carboxy ^{13}C signals of crystalline sodium [1-^{13}C]acetate and of potassium [1-^{13}C]acetate in CHA, respectively. Spinning sidebands (s.s.b.) of the C-1′ in B were minimized by multiplying one spectrum by another taken at a different spinning rate. ^{13}C Shifts of sodium benzenesulphonate (shifts in parentheses are from aqueous solution): C-1′; 169.3 (142.9), C-2′; 123.8 (122.7), C-3′; 131.4 (129.3); C-4′, 144.0 (131.8) p.p.m.

respectively); ^{13}C shifts in gel and solid states are determined by fixed values of these dihedral angles, while those in aqueous solution are time-averaged as a result of rapid conformational isomerism about the glycosidic linkages.

Here we report the first ^{13}C n.m.r. study of crystalline cyclohexa-amylose (CHA) inclusion complexes by the cross polarization–magic angle spinning (CP–MAS) technique[2] to obtain further information about the conformation-dependent ^{13}C shifts and hopefully to relate this to the dihedral angles determined by *X*-ray crystallography.[3]

Figure 1 illustrates ^{13}C CP–MAS n.m.r. spectra of some CHA inclusion complexes. Crystalline samples enclosing guest molecules appear to give narrowed peaks which split into several peaks in the C-1 and C-4 regions. These ^{13}C peaks were readily assigned when compared with the range of shifts of CHA and amylose in aqueous solution;[1c] they are summarized in Table 1. ^{13}C Shifts of acetate, ethanol, and propan-1-ol as the guests (primed carbon atoms) are not significantly displaced from those found in solution. However, the ^{13}C signals of the C-1′ and C-4′ carbons of the benzenesulphonate group in the complex are substantially displaced downfield (−26 and −12 p.p.m., respectively) compared with those in aqueous solution (pH 7).

It is convenient to discuss the ^{13}C shifts of CHA by dividing its inclusion complexes into two groups, one containing symmetrical adducts (with approximate six-fold symmetry) and the other, asymmetrical (deformed structure) complexes. The dihedral angles of the symmetrical complexes enclosing potassium acetate[3b] and sodium benzenesulphonate[3e] are 169 ± -1.2 and $-171.2 \pm 2°$ for ϕ and ψ, respectively, whereas those of the asymmetrical ones enclosing H_2O,[3d] methanol,[3c] and propan-1-ol[3a] are broadly distributed in the

Table 1. ^{13}C Chemical shifts of crystalline cyclohexa-amylose inclusion complexes (p.p.m. from Me_4Si, ± 0.5 p.p.m.)

	Crystalline inclusion complexes								Amylose[b]		
	Symmetrical			Asymmetrical							
	Potassium acetate	Sodium benzene-sulphonate	Dihedral angles[a]	H_2O	Methanol	Ethanol	Pro-pan-1-ol	Dihedral angles[a]	V-amylose	Dihedral angles[a]	Aqueous soln.
C-1		101.9		102.1	102.3	102.7	102.7	160 ± 2°[d]	102.6	164.6°[e]	100.3
	100.3	100.7	169 ± 1°[c]	99.3	99.7	99.9	100.4	169 ± 7°[d]			
C-4				81.1	82.3	82.1	81.4	−183 ± 7°[d]	82.4	−186.1°[e]	77.9
	80.9	80.1	−171 ± 2°[c]		80.7	80.5	80.4	−168 ± 9°[d]			
				75.6	75.6	76.2	75.7	−150 ± 5°[d]			
C-6	61.1	62.1	g^+t	60.7	60.3	60.1	60.6	g^-g^+	62.4	g^+t	61.4
C-3	72.6	73.6		72.6	73.0	73.6	73.1		73.2		74.2
C-2											72.4
C-5					71.6	72.0	71.5				72.0

[a] The dihedral angles for the C-1 and C-4 shifts are given by the ϕ and ψ, respectively (for definitions, see ref. 3a). The angle for the C-6 shift is given by either g^+t or g^-g^+ orientation. [b] ^{13}C Shift data taken from ref. 1c. [c] Taken from refs. 3b and 3e. [d] Taken from refs. 3a, 3c, and 3d. [e] Taken from ref. 4.

following two or three regions: $\phi = 160 \pm 2$ and 169 ± 7°, and $\psi = -183 \pm 7$, −168 ± 9, and −150 ± 5°. The appearance of two or three peaks is consistent with this distribution of the dihedral angles. Thus, it is reasonable to ascribe the individual C-1 and C-4 signals to the glucose residues adopting different dihedral angles in the crystals. In a similar manner, we ascribed the C-6 signals to either g^-g^+ (asymmetrical crystals[3a,c,d]) or g^+t (symmetrical crystals[3b,e] and V-amylose[1]) forms as viewed from the C-6–O-6 orientation with respect to C-4–C-5 and O-5–C-5 bonds. As summarized in Table 1, these correlations seem to be generally good, although they are not quantitative at present.

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