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^{13}C-N.M.R. STUDY OF THE CONFORMATION OF HELICAL COMPLEXES OF AMYLODEXTRIN AND OF AMYLOSE IN SOLUTION*

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ABSTRACT

Amylose (average d.p. 1000) and amylodextrin (average d.p. 25) have identical ^{13}C-n.m.r. spectra, except for some minor signals from the small amount of α-1→6 branch linkages present in amylodextrin. Amylodextrin can be obtained as stable solutions in much higher concentrations than amylose and so requires only 1/100th as many scans to obtain a spectrum comparable to that of amylose. ^{13}C-N.m.r. spectroscopy has been used to study the formation of amylodextrin complexes with organic complexing agents in aqueous solution. A control study using dextran, which does not form helical complexes, showed that, when complexing agents are added, the signals from all of the carbons show a slight downfield shift due to a general solvent effect. In the case of amylodextrin, the addition of increasing concentrations of complexing agent also produced a downfield shift of the signals of all the carbons, but there was a greater shift of the signals for carbons 1 and 4 than for carbons 2, 3, and 6, indicating that something more than a solvent effect was occurring. The cycloamyloses (cyclic α-1→4 linked D-glucose oligosaccharides which may be considered as model for an amylose helix) in water have chemical shifts for carbons 1 and 4 that are comparable to those shown by the amylodextrin complexes. It is thus proposed that the formation of a helical complex with amylodextrin results in a change in the conformation of the glycosidic linkage, which is reflected by greater downfield shifts of the signals for carbons 1 and 4, relative to those for carbons 2, 3, and 6. It was observed that differences in the ratio of the downfield shifts of C-1 and C-4 of the different amylodextrin complexes indicate differences in the degree of compactness of the helical structures. A comparison of the ^{13}C chemical shifts of methyl α-D-glucoside and methyl α-mal-

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toside showed that, for a molecule as small as a disaccharide, there is a conformational change about the glycosidic linkage when complexing agents are added.

INTRODUCTION

A helical structure for starch chains was first proposed by Hanes[1] in 1937 to explain the formation of specific products from the action of malt α-amylase. Freudenberg *et al.*[2] adopted the helical model because it was consistent with the cyclic structure of the Schardinger dextrins. In 1943, Rundle and co-workers presented the first experimental evidence for the existence of the helical structure of amylose in their studies of the flow dichroism[3] and X-ray diffraction of the amylose–iodine complex[4–7]. Since then, many other helical amylose complexes, such as amylose–fatty acid[8,9], amylose–*n*-butyl alcohol[5,10–12], amylose–*tert*-butyl alcohol[13,14], amylose–dimethyl sulfoxide[15–17], and amylose–α-naphthol[18], have been reported and investigated. All these are known as amylose-V complexes[19], and all have a pitch of about 0.8 nm, which indicates that the coils of the helix are in contact with each other. There also are extended amylose helical complexes, such as amylose–KOH[20–22] and amylose–KBr[23,24] complexes.

Methods that have been commonly used to study the structures of amylose complexes are X-ray crystallography[4–24] and light[25,26] or electron microscopy[10,11,13,18]. All are restricted to the study of crystalline structures. French *et al.*[26] developed a method for surveying the ability of various organic compounds to form amylose complexes by observing the formation of amylose precipitates, a method that was further applied by Kuge and Takeo[27]. This method, however, fails to detect some water soluble complexes, such as the amylose–dimethyl sulfoxide and amylose–KOH complexes, and has led to inconsistent results from different laboratories. Viscometry also has been used to study the formation of amylose complexes in solution[28,29]. The increase in viscosity of amylose in alkaline solution was misinterpreted as evidence for a random coil conformation instead of an extended helix[20–22].

Formation of helical amylose complexes should involve conformational change, principally of the glycosidic linkage, as the amylose molecule is converted from a random coil to a helix. Changes in the torsion angles of a glycosidic linkage will affect the pattern of electron distribution about the linkage. Therefore, a change in conformation can be detected by nuclear magnetic resonance (n.m.r.) as a change in the electronic shielding of the atoms involved in the linkage. Because of the fast exchange rate of hydroxyl protons, the usefulness of proton n.m.r. is limited. On the other hand, ^{13}C-n.m.r. should be an effective probe of the conformation of amylose in solution.

Dorman and Roberts[30] reported that amylose in M potassium hydroxide solution exhibited downfield chemical shifts when compared with amylose in neutral solution. This shift was misinterpreted as a disruption of the helical conformation, on the basis of the then proposed random coil conformation of amylose in alkaline

solution, which was later shown to be incorrect[20]. In the present study, we have found a specific pattern of downfield shifts for C-1 and C-4 (the carbons involved in glycosidic bonds) when amylodextrin helical complexes are formed. The shifts are similar to those observed for the amylose–KOH extended helical conformation.

MATERIALS AND METHODS

Chemicals. — Amylodextrin (d.p. 25) was prepared by prolonged acid hydrolysis of potato starch[31,32] (16% sulfuric acid for 3 months), from which fraction II, used in the experiments, was obtained by gel filtration on Sephadex G-50 (ref. 40). Fraction II was recrystallized from methanol twice before use. When dissolved in hot water at a concentration of 50 mg/mL it gave a clear and stable solution.

Methyl α-D-glucopyranoside was available in the laboratory. Methyl α-maltoside was prepared by the action of *Bacillus macerans* transglycosylase on methyl α-D-glucoside and cyclomaltohexaose[33], and separated by charcoal column chromatography[34]. Triiodide reagent was prepared by dissolving 200 mg of iodine and 260 mg of potassium iodide in 1 mL of distilled water. α-Naphthol was recrystallized before use. Other chemicals were reagent grade and were used without further treatment.

Leuconostoc mesenteroides B-512F dextran (mol. wt. about 4×10^7) and dextran T-10 (mol. wt. 5200) were obtained from Sigma Chemical Co., St. Louis, MO.

Amylodextrin solutions. — Complexing agents (or other compounds) were added to amylodextrin solutions (50 mg/mL) as these were being stirred in a boiling water bath, and then the solutions were slowly cooled to 24°. Measured volumes of dimethyl sulfoxide (DMSO) and water were added separately to amylodextrin solutions in water or DMSO, with heating and stirring, to prepare samples having known ratios of DMSO to water.

^{13}C-N.m.r. spectroscopy. — Nuclear magnetic resonance experiments were carried out on a Bruker WM-300 spectrometer operated at 75 MHz for the observation of ^{13}C. During data acquisition, proton resonances were broad-band decoupled. ^{13}C-Chemical shifts, quoted in p.p.m. from tetramethylsilane, were measured by reference to external dioxane at 66.5 p.p.m. For aqueous samples the water used as solvent contained 20% D_2O for field–frequency lock, and similarly when DMSO* was the solvent, 20% of DMSO-d_6 was added. The assignment of the carbon resonances of methyl α-maltoside was accomplished by ^{1}H *J*-resolved 2-D n.m.r., ^{1}H chemical shift correlated 2-D n.m.r., and ^{13}C–^{1}H chemical shift correlated 2-D n.m.r.

RESULTS

^{13}C-N.m.r. spectra of aqueous solutions of potato amylose (d.p. 1000) and amylodextrin (d.p. 25). — The highest concentration of potato amylose (d.p. 1000)

*Dimethyl sulfoxide.

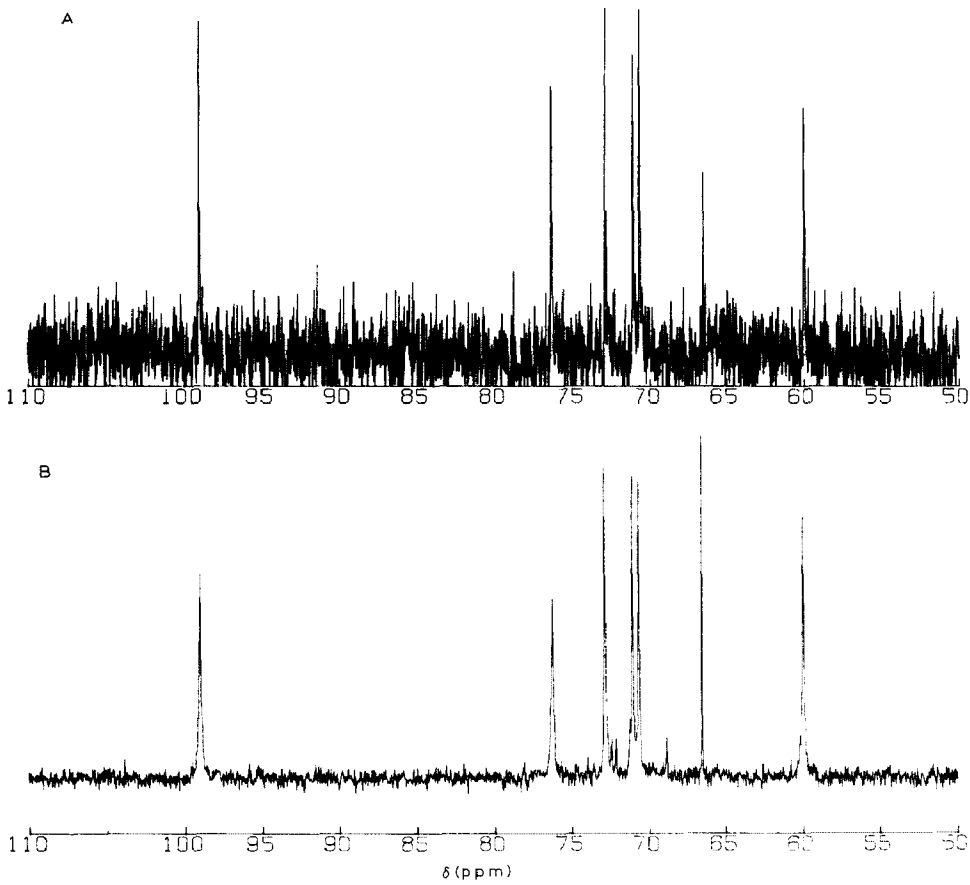

Fig. 1. A, ^{13}C-N.m.r. spectrum of amylose in aqueous solution. Amylose was first dissolved in DMSO (33 mg/mL). A portion of the solution was then diluted to 1 mg/mL with 20% D_2O in H_2O. The spectrum was obtained after 26,000 scans at 25°. B, ^{13}C-N.m.r. spectrum of amylodextrin (d.p. 25) in aqueous solution (50 mg/mL), obtained after 256 scans at 25°.

that gives a stable aqueous solution at room temperature is about 1 mg/mL. A ^{13}C-n.m.r. spectrum of aqueous amylose at this concentration is shown in Fig. 1A. This spectrum is the result of 26,000 scans, collected over 12-hour period. Amylodextrin with an average d.p. of 25, on the other hand, gives stable aqueous solutions at concentrations as high as 50 mg/mL. A ^{13}C-n.m.r. spectrum of such a solution, obtained after only 256 scans (Fig. 1B), had much decreased baseline noise. The major peaks, however, are identical with those of Fig. 1A. The very minor signals that appear in the region of δ 68–74, specifically δ 69, δ 72, and δ 72.5 (see Fig. 2), correspond to a small amount of α-1→6 branch linkages. Amylodextrin (fraction II) is known to contain one branch linkage per molecule, located near the reducing end[40].

^{13}C-N.m.r. spectra of solutions of amylodextrin-V complexes. — Compounds reported to give amylose-V complexes (DMSO, potassium triiodide, *n*-butyl

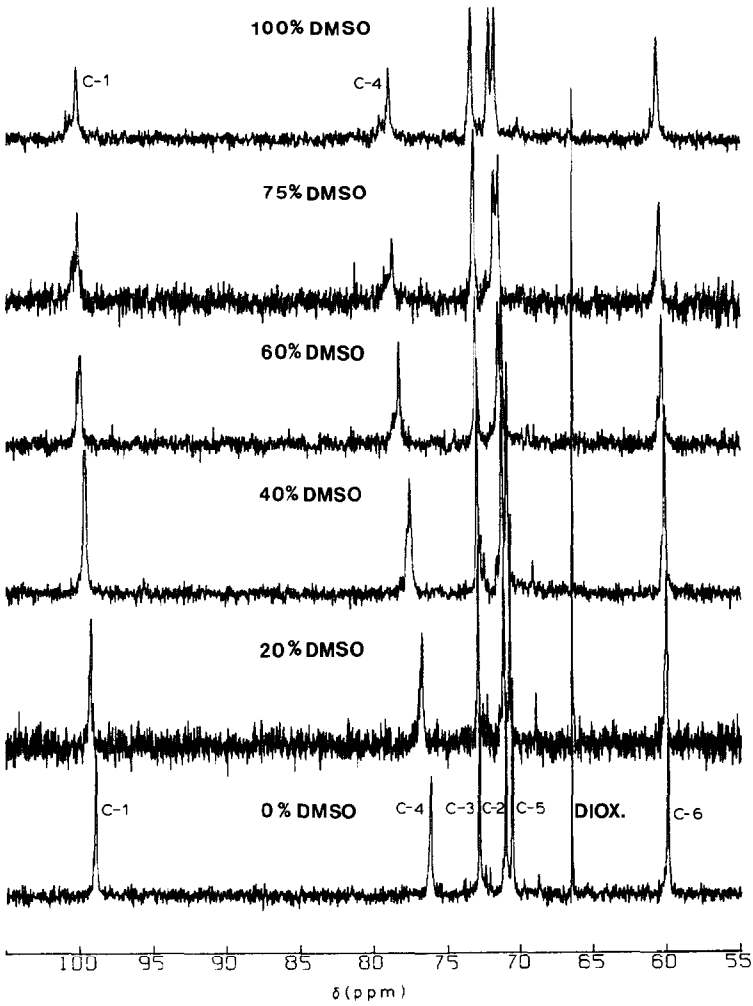

Fig. 2. ^{13}C-N.m.r. spectra of amylodextrin in aqueous solutions with added DMSO. Identical spectra were obtained after back titration of an amylodextrin–DMSO solution with water.

alcohol, *tert*-butyl alcohol, α-naphthol, methyl alcohol, and cyclohexanol) were used to titrate amylodextrin solutions. Spectra of amylodextrin solutions containing different proportions of DMSO are shown in Fig. 2. The chemical shifts of each carbon atom are plotted against the concentration of DMSO[35] in Fig. 3. These plots show that carbons 1 and 4, which are involved in the glycosidic bonds, are shifted downfield more than the other carbons by the addition of DMSO. The same chemical shift behavior was observed on the addition of triiodide or any of the other complexing agents named above (data not shown). The ratio of the change in the chemical shift of carbon 1 to that of carbon 4 upon addition of a complexing agent ($\Delta\delta_{C-1}/\Delta\delta_{C-4}$) is 0.6 for all complexing agents except DMSO, for which a ratio of 0.51 was obtained.

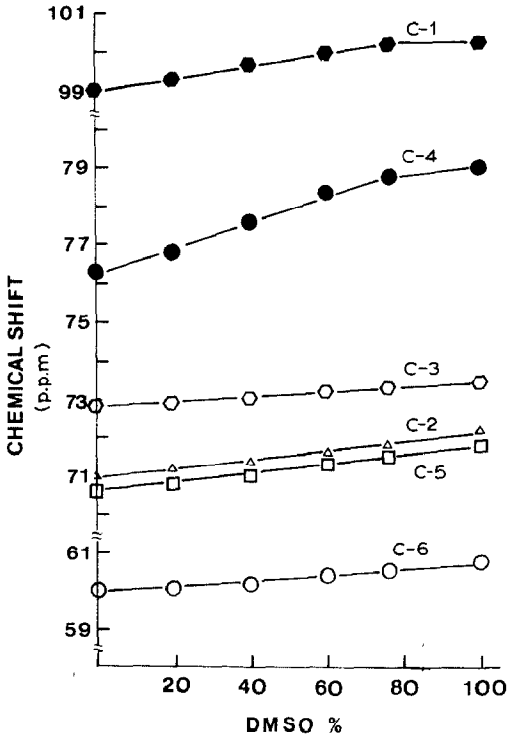

Fig. 3. ^{13}C-Chemical shifts of amylodextrin in solutions containing various proportions of water and DMSO, plotted from the spectra shown in Fig. 2.

^{13}C-N.m.r. spectra of solutions of an amylodextrin extended-helix complex. — When potassium hydroxide is added to an amylodextrin solution, the signals for carbons 1 and 4 also move downfield (Fig. 4). The ratio of shift changes, $\Delta\delta_{C-1}/\Delta\delta_{C-4}$, is 0.75.

Effect of helix to random coil transition on the ^{13}C-n.m.r. spectra of amylodextrin solutions. — An aqueous solution of amylodextrin gave the ^{13}C-n.m.r. spectrum shown in Fig. 5A. When triiodide was added to the amylodextrin solution, the solution turned purple, which indicates the formation of an amylodextrin–triiodide complex. The ^{13}C-n.m.r. spectrum of this complex is shown in Fig. 5B; the signals of carbons 1 and 4 move downfield and broaden. The same purple solution was then titrated with 0.04N sodium thiosulfate until the color disappeared. The ^{13}C-n.m.r. spectrum of the resulting solution (Fig. 5C) shows that the signals for carbons 1 and 4 again become sharp, and their positions are the same as in the spectrum taken in the absence of triiodide (Fig. 5A).

^{13}C-N.m.r. spectra of methyl α-D-glucoside and methyl α-maltoside and their complexes with DMSO. — Methyl α-D-glucoside and methyl α-maltoside were used as model compounds for complex formation. Upon the addition of DMSO to an aqueous solution of methyl α-D-glucoside, the signals for all the D-glucose carbons

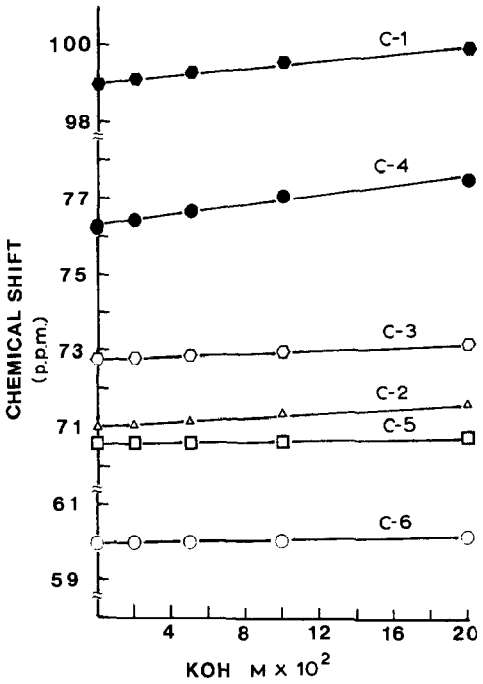

Fig. 4. ^{13}C-Chemical shifts of amylodextrin in aqueous solution, in the presence of various concentrations of KOH.

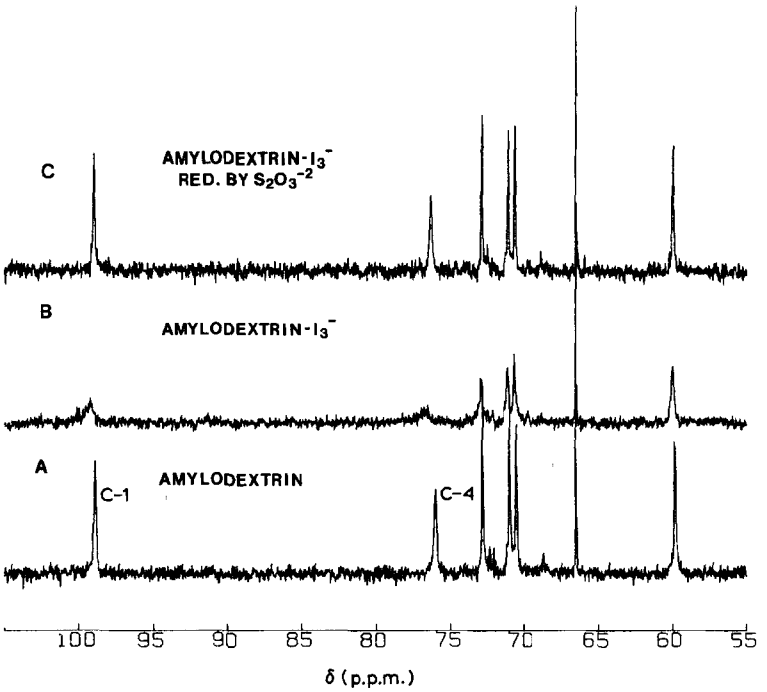

Fig. 5. A, ^{13}C-N.m.r. spectrum of amylodextrin in aqueous solution. The peaks, from left to right, are assigned to C_1, C_4, C_3, C_2, C_5, dioxane, and C_6. B, ^{13}C-N.m.r. spectrum of amylodextrin–triiodide complex in aqueous solution. C, ^{13}C-N.m.r. spectrum of the solution used in B, after addition of sufficient 0.04N sodium thiosulfate to destroy the purple color.

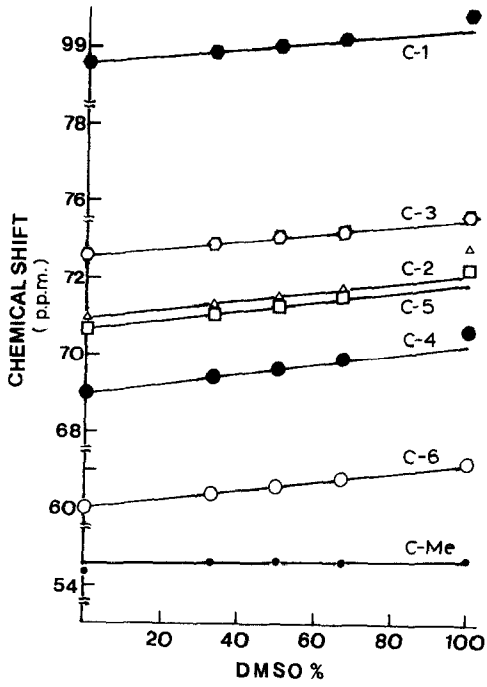

Fig. 6. ^{13}C-Chemical shifts of methyl α-D-glucoside in aqueous solution in the presence of various concentrations of DMSO.

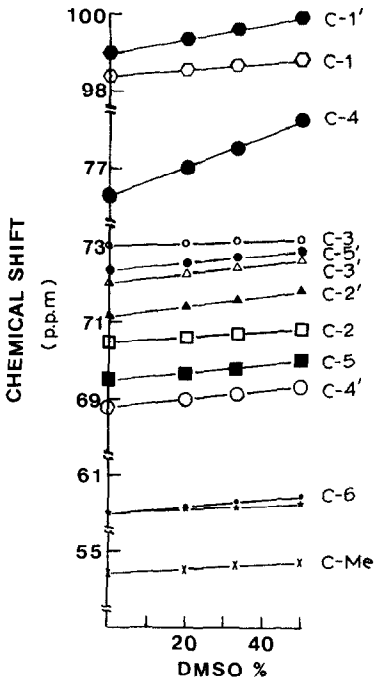

Fig. 7 ^{13}C-Chemical shifts of methyl α-maltoside in aqueous solution in the presence of various concentrations of DMSO.

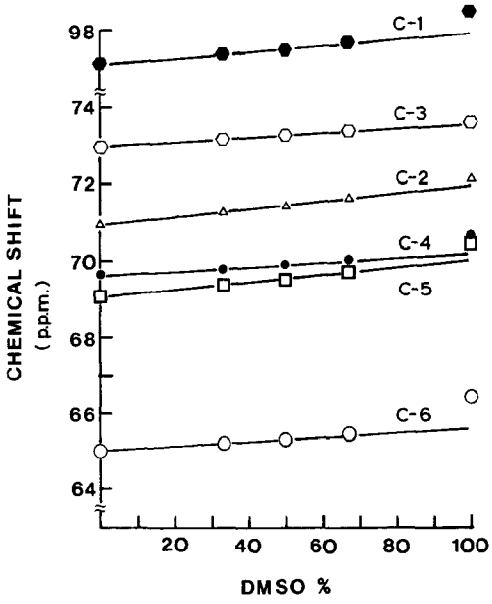

Fig. 8. ^{13}C-Chemical shifts of dextran T-10 in aqueous solution in the presence of various concentrations of DMSO.

showed parallel downfield shifts (Fig. 6). However, methyl α-maltoside in the presence of varying concentrations of DMSO gave a different pattern of changes. The signals of carbons 1′ and 4, in particular, exhibited marked downfield shifts with increasing DMSO concentration (see Fig. 7).

^{13}C-N.m.r. spectra of amylodextrin in the presence of compounds that do not form complexes. — Amino acids, hexane, and sucrose are known not to form complexes with amylose. L-Glutamic acid, L-tyrosine, hexane, and sucrose were added (separately) to amylodextrin solutions, but these additions caused no changes in the chemical shifts of the amylodextrin signals (data not shown).

^{13}C-N.m.r. spectra of dextran solutions containing DMSO or ethanol. — Solutions of dextran T-10 (M_n = 5,200) in water, DMSO, and mixtures of these two solvents were prepared. The spectra of these solutions show parallel changes in chemical shift with increasing DMSO concentration for all dextran carbons (Fig. 8). Addition of up to 20% (v/v) ethanol to aqueous solutions of the native dextran of *Leuconostoc mesenteroides* B-512F gave the same pattern of chemical shift changes.

^{13}C-N.m.r. spectra of aqueous solutions of cyclodextrins and their complexes with DMSO. — In the ^{13}C-n.m.r. spectra of aqueous cyclomaltohexaose and cyclomaltoheptaose the chemical shifts of carbons 1 and 4 are greater than the corresponding shifts for amylodextrin in water solution (Table I). The chemical shifts of carbons 1 and 4 of the cyclodextrins, however, are comparable to those observed for carbons 1 and 4 of amylodextrin in the helical complex formed in 75% DMSO.

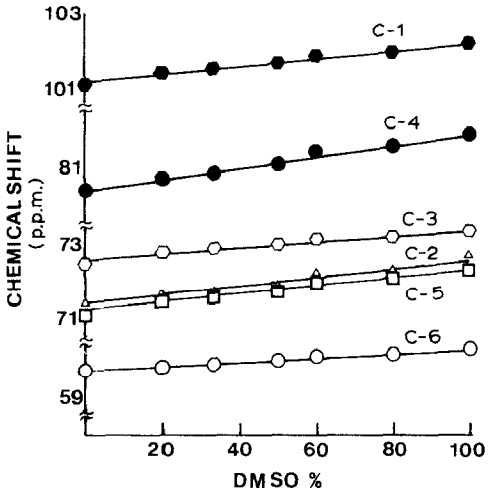

Fig. 9. ^{13}C-Chemical shifts of cyclomaltoheptaose in aqueous solution in the presence of various concentrations of DMSO.

The addition of DMSO to aqueous solutions of the cyclodextrins causes larger downfield changes in the shifts of carbons 1 and 4 than in the shifts of the other carbons (Fig. 9), but these changes are not as great as those observed for carbons 1 and 4 of amylodextrin (compare Fig. 3 with Fig. 9).

DISCUSSION

The ^{13}C-n.m.r. spectrum of d.p. 25 amylodextrin shows that each glucose carbon has the same chemical shift as the glucose carbons of native potato amylose (d.p. 1000), except for the minor signals of the α-1→6 branch linkage that appear

TABLE I

^{13}C-CHEMICAL SHIFTS OF AMYLODEXTRIN, CYCLOMALTOHEXAOSE, AND CYCLOMALTOHEPTAOSE IN WATER AND 75% DMSO SOLUTIONS

Carbon	*δ (p.p.m. from tetramethylsilane)*					
	Amylodextrin		*Cyclomaltohexaose*		*Cyclomaltoheptaose*	
	H_2O	*75% DMSO*	*H_2O*	*75% DMSO*	*H_2O*	*75% DMSO*
1	98.93	100.2	100.81	101.75	101.11	101.92
4	76.15	78.73	80.63	81.83	80.39	81.44
3	72.78	73.25	72.84	73.32	72.44	73.12
2	70.99	71.80	71.44	72.00	71.43	72.34
5	70.56	71.44	71.19	71.62	71.08	72.04
6	59.91	60 48	59.87	60.16	59 64	60.10

in the region of δ 68–74. The spectrum of amylodextrin, however, can be obtained in only 1/100th the acquisition time required for native amylose. A linear amylodextrin chain of 25 residues can form 3 or 4 turns of a helix with 6 to 8 D-glucose residues per turn. The experiments described in this study were conducted to investigate the effect on the ^{13}C-n.m.r. spectrum of the transition from a random coil conformation in aqueous solution to the helical conformation characteristic of amylodextrin complexes. The changes observed in the spectrum upon the addition of complexing agent to amylodextrin should also occur upon the addition of the same complexing agent to amylose. These changes are due to local conformational changes. Thus, a study of amylodextrin of d.p. 25 fulfills the same purpose as a study of amylose, but is accomplished at a much higher concentration (50 mg/mL *vs.* 1 mg/mL) and therefore with many fewer spectral scans (256 *vs.* 26,000).

The spectra of the complexes formed by the addition of DMSO (Figs. 2 and 3), triiodide, alcohols, etc., to aqueous amylodextrin show a marked downfield movement of the signals of carbons 1 and 4, with little change in the positions of the other carbon signals. The changes in the ^{13}C-n.m.r. spectra of amylodextrin upon addition of complexing agent can be reversed by the chemical destruction of the complexing agent, as shown by the experiment with the triiodide complex, or by raising the temperature of the solution.

The downfield shift of the signal of a given nucleus results from local deshielding by either a change in charge density[36] or bond polarization[37,38]. The formation of an amylodextrin-V complex from random coil amylodextrin requires rotations about the two carbon-oxygen bonds of the glycosidic linkages, resulting in a different steric environment around carbons 1 and 4. We propose that these changes in steric relationships are the cause of the observed specific deshielding of these carbons.

The splitting of the signals of carbons 1, 4, and 6 of the amylodextrin in the presence of high concentrations of complexing agent (see Fig. 2) is due to the presence of a single α-1→6 branch linkage in each amylodextrin molecule[39]. The branch linkage is located near the reducing end[40]. The two chains resulting from the branch linkage in the molecule will individually form helical complexes with the complexing agent. The D-glucose residue to which the branch linkage is attached and those D-glucose residues adjacent to the branch linkage suffer a strain when the helices are formed, due to their inability to participate in the helical structures. This strain results in a distortion of the torsion angles, with the consequent shift of the signals from carbons 1, 4, and 6 of these D-glucose residues. When the concentration of the complexing agent is low, the helices are not completely formed, and the splitting of the signals is not observed. In the presence of high concentrations of complexing agent, however, the helices are completely formed and the splitting is observed. In addition, the carbons of D-glucose residues at the nonreducing ends have different chemical shifts from those of interior D-glucose residues in the helical chain, as can be seen from the data for methyl α-maltoside in the presence of complexing agent (Fig. 7). Thus, two factors contribute to the splitting of the signals of carbons 1, 4, and 6.

The chemical shifts of the signals from carbons 1 and 4 of amylodextrin after the addition of complexing agents are similar to those of carbons 1 and 4 for pure cyclodextrins in water solution (see Table I). On the addition of complexing agents to the cyclodextrins there is a further downfield shift due to the relatively small conformational changes involved in the formation of the cyclodextrin complexes. The fixed cyclic structure of the cyclodextrins makes them useful model compounds for the helical, amylose-V complexes. The observed torsion angles, ϕ and ψ, in the cyclodextrins[41,42] compare closely with the corresponding angles in amylose-V complexes[19]. We interpret the similarity in the ^{13}C-n.m.r. spectral behavior of cyclodextrins and amylodextrin-V complexes as further evidence that changes in the torsion angles are responsible for the observed downfield shifts of the signals of the glycosidically bound carbons in these molecules. The chemical shifts of peptide-linkage carbons in L-proline oligomers display similar changes upon the addition of lithium and calcium salts, which alter the conformation of these peptides[43,44].

The possibility that the greater chemical shifts of carbons 1 and 4 were due to general solvent effects on the glycosidic linkage was studied by using *Leuconostoc mesenteroides* B-512F dextran, a predominantly α-1→6 linked glucan, as a test material. This dextran may be precipitated from aqueous solution by increasing the ethanol concentration to 36% or higher[45], which is similar to the ethanol precipitation of amylose. Dextran, however, does not form helical complexes with any of the agents used to form amylose complexes. If the greater downfield shifts of the signals of carbons 1 and 4 of amylodextrin were due to general solvent effects rather than the conformational changes accompanying a random coil to helix transition, dextran solutions should also display an increase in the chemical shifts of carbons 1 and 6 relative to the other carbons when the various agents are added. The ^{13}C-n.m.r. spectrum of dextran in 20% ethanol shows parallel downfield displacements of the chemical shifts for all six carbons (data not shown). The same pattern is observed for dextran T-10, a low molecular weight dextran with a d.p. of 32, when DMSO is added (see Fig. 8). In none of the dextran spectra were the signals for carbons 1 and 6 displaced more than those of the other carbons. This finding eliminates the possibility that the relatively greater increase of the chemical shifts of carbons 1 and 4 of the amylodextrin complexes is caused by general solvent effects on the glycosidic linkage. Dextran does not go through any specific conformational changes when ethanol or DMSO is added. The addition of ethanol produces dextran aggregation and precipitation by decreasing the hydrophilic character of the solvent.

The amylodextrin-V complex exists as a collapsed helix, in which the complexing agent is in the cavity of the helix and adjacent turns of the helix are in physical contact[19]; this is not the case for the extended helix of the amylodextrin–KOH complex[20–22]. This difference in conformation is reflected in the differences of the ratios of the downfield shifts of the C-1 and C-4 signals: $\Delta\delta_{C-1}/\Delta\delta_{C-4}$ for the KOH complex is 0.75 (Fig. 4), compared with 0.6 for the V complexes. The amylodextrin–DMSO complex downfield shift ratio is 0.51 (Fig. 3). This latter difference, perhaps, is due to an even more compact helix.

Increases in the concentration of DMSO, in an aqueous solution of methyl α-D-glucoside, cause a parallel downfield change in the chemical shifts of all six glucose carbons (Fig. 6). The fact that the methyl carbon signal does not move indicates there are no conformational changes involving this glycosidic bond. Instead, DMSO may cause distortion of the pyranose ring through a chelating-like, hydrogen-bonding and hydrophobic interaction, leading to the downfield shifts of the signals for the D-glucose carbons.

When DMSO is added to a solution of methyl α-maltoside, a series of ^{13}C-n.m.r. spectra showing characteristics of both methyl α-D-glucoside and amylodextrin is obtained (Fig. 7). Carbons 1′ and 4 show downfield shift changes like those seen in amylodextrin spectra, suggesting that DMSO induces rotations about the 1′→4 linkage similar to those involved in amylodextrin-V complex formation. A reduced downfield shift of the resonances of the four carbons (C-2, C-3, C-5, and C-6) of the first residue of methyl α-maltoside is similar to the downfield shifts of the same four resonances of the glucopyranosyl residues in amylodextrin. The reduction of these downfield shifts, in contrast to the shifts observed for methyl α-D-glucoside and the nonreducing residue of methyl α-maltoside, may be attributed to the release of tension on the C-4-substituted glucopyranose ring. This tension is induced by the interaction of the ring with the complexing agent, and is reduced primarily by rotation about the ψ bond of the glycosidic linkage. We conclude that all of the properties of amylose, which lead to complex formation, may be present in a simple molecule consisting of two glucose residues linked α-1→4. This conclusion is consistent with an observation made by Thoma and French that, at 0.2°, triiodide binding by maltose could be detected potentiometrically[46].

Another important feature of the ^{13}C-n.m.r. spectra of amylodextrin taken during titration with complexing agents is that each carbon gives only one signal. The change in the chemical shift of each carbon is proportional to the concentration of the complexing agent. This behavior is consistent only with a rate of interconversion between two states that is fast enough to give a time-averaged spectrum; two distinct spectra would be expected in the case of a slow interconversion[47]. This shows that the amylodextrin-V complexes are in fast dynamic equilibrium with free amylodextrin, and is consistent with observations on the lamellae formed by amylose–alcohol complexes[13].

Compounds that do not form helical complexes with amylose, such as hexane and the amino acids L-glutamic acid and L-tyrosine, have no effect on the chemical shift of any of the amylodextrin carbons at any concentration. This observation reinforces our hypothesis that the excess downfield shifts observed for carbons 1 and 4 relative to carbons 2, 3, and 6, when complexing agents are added to amylodextrin solutions, are due to conformational changes associated with the formation of a helix. Benzoic acid, which previously was reported not to form a precipitate with amylose and, hence, not to form a helical complex[27], gives a spectrum identical to those of other amylodextrin-V complexes. We thus believe that benzoic acid forms a helical complex with amylose and that the ^{13}C-n.m.r. spectrum

is a better index of complex formation than is the formation of a water-insoluble precipitate.

X-Ray studies of the interaction of cyclomaltohexaose and cyclomaltoheptaose with various molecules show that complexes are formed by the binding of the complexing agent in the cavity of the cyclodextrin. The observed downfield displacements of the signals for carbons 1 and 4 are due to this complex formation. The changes, however, are much smaller than those seen for amylodextrin (compare Figs. 3 and 9 and Table I). These differences may be explained by the relatively rigid structures of the cyclodextrins, in which only slight conformational changes are permitted in contrast to amylodextrin and amylose, which can undergo random coil to helix transitions.

In summary, ^{13}C-n.m.r. studies have shown that when complexing agents are added to aqueous amylodextrin solutions, there is a downfield change in the chemical shifts of carbons 1 and 4 of the D-glucopyranose residues of the amylodextrin. This change has been interpreted as a change in the torsion angle of the α-1→4 glycosidic linkage, which is due to the formation of a helical structure. Differences in the ratio of the downfield shifts of carbons 1 and 4 will distinguish an extended helix from a compact helix. The ^{13}C-n.m.r. spectra of methyl α-D-glucoside and methyl α-maltoside provide evidence that a molecule as small as a disaccharide will form a complex with agents such as DMSO.

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