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Note

Conformational change of the β-D-glucan of *Auricularia auricula-judae* in water–dimethyl sulfoxide mixtures

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A polysaccharide designated β-D-glucan A, extracted from the plant *Auricularia auricula-judae* with 70% ethanol and then with aq 1% NaCl, has a backbone chain of (1 → 3)-β-D-glucose residues, two out of three glucose residues being substituted at O-6 by single glucosyl groups [1]. Measurements by light scattering, membrane osmometry, and viscometry show that the β-D-glucan A dissolves as a single-stranded helical structure in water and as a semi-flexible chain in dimethyl sulfoxide (Me_2SO) [2]. Analysis of the data in terms of Yamakawa–Fujii–Yoshizak theory yielded 1030 ± 100 nm^{-1}, 90 ± 20 nm, 1.3 ± 0.3 nm, and 0.26 ± 0.03 nm for the molar mass per unit contour length M_L, persistence length q, diameter d, and contour length h per main-chain glucose residue of glucan A in water, and 19 ± 5 nm for q and 1.3 ± 0.3 nm for d in Me_2SO, which was considered to indicate semi-flexibility. In this work, intrinsic viscosities $[\eta]$, number-average molecular weights M_n, and second virial coefficients A_2 of the glucan A were investigated as functions of w_{Me_2SO} (the mass fraction of Me_2SO in water–Me_2SO mixtures). The M_n value is relative to the total number of molecules present, and so it can reflect changes in single- or multiple-stranded structure.

1. Experimental

Preparation of solutions.—The glucan A was isolated from the fruit body of *Auricularia auricula-judae* by the previously described method [1].

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The fruit was cultivated in Fangshan (Hubei, China). The sample of glucan A, having weight-average molecular weight M_w 117 × 10^4 [1], was dissolved directly in water–Me_2SO mixtures of desired composition (w_{Me_2SO} from 0 to 1) at room temperature. The solutions thus prepared were kept for one day, and then used for measurements. Also used was a water-diluted Me_2SO solution prepared by dissolving the sample in Me_2SO and then diluting it with water (w_{Me_2SO} from 1 to 0.4).

Membrane osmometry.—Osmotic pressures (π) of the sample in water, Me_2SO, and water–Me_2SO mixtures were measured with an improved Bruss membrane osmometer by rapid static equilibrium at 25 ± 0.05°C [3]. The M_n and A_2 values of the glucan A for a given w_{Me_2SO} were obtained from the intercept and slope of a plot of π/c against concentration (c).

Viscometry.—Zero shear-rate viscosities of the sample in water, Me_2SO, and water–Me_2SO mixtures were determined by linear extrapolation with a low-shear two-bulb capillary viscometer supplied by the Beijing Chemistry Institute of Academic Sinica. Huggins and Mead–Fuoss plots were used to estimate the intrinsic viscosity $[\eta]$ and the Huggins constant k' of the glucan A sample in the aforementioned solvent.

2. Results and discussion

The M_n and A_2 values for the glucan A sample in water–Me_2SO mixtures at 25°C are given in Table 1 and are plotted against w_{Me_2SO} in Fig. 1. Over the whole range of w_{Me_2SO} from 0 to 1, the values of M_n do not change appreciably. However, the values of A_2 increase smoothly with increasing w_{Me_2SO} from 0 to 1, indicating an increase of interaction between the glucan A molecules and Me_2SO molecules of water–Me_2SO mixtures. These results indicate the absence of multiply stranded structures that could be dissociated in Me_2SO or water–Me_2SO mixtures, suggesting that single-stranded chains of glucan A are maintained in water, Me_2SO, or water–Me_2SO mixtures. The w_{Me_2SO} dependences of M_n and A_2 of the glucan A differ from both the triple-stranded helix of schizophyllan [4] and the double-stranded helix of xanthan [5]. The M_w value of schizophyllan in water was ca. three times larger than that in Me_2SO, and $[\eta]$ and k' in a very narrow w_{Me_2SO} range around 0.87 all decreased to the values observed in pure Me_2SO. This demonstrated that the triple helix of schizophyllan dissociated abruptly to

Table 1
Experimental results for osmotic pressure and viscosity for glucan A in water–Me_2SO mixtures

w_{Me_2SO}	$[\eta]\times10^{-3}$ (mL/g)	k'	$M_n\times10^{-4}$	$A_2\times10^4$ (mL mol/g^2)
0	4.95	0.49	23.9	4.5
0.2	5.40	0.43		
0.3			21.1	4.8
0.4	4.40	0.39		
0.6	4.10	0.40	22.2	5.1
0.8	2.35	0.39		
1.0	0.82	0.37	23.4	5.3

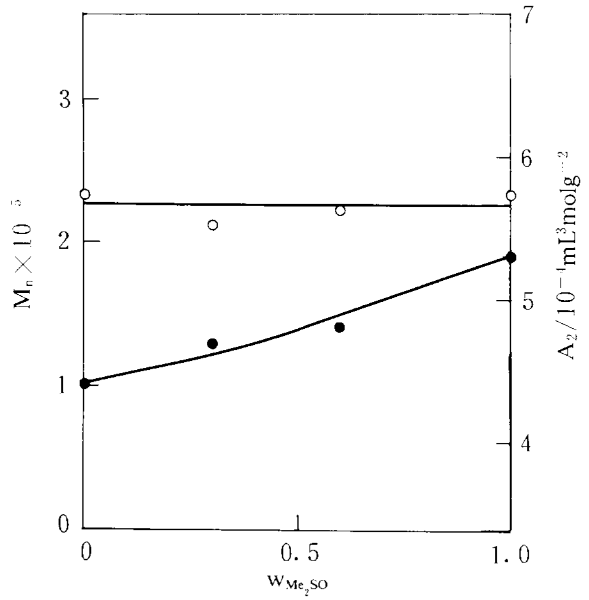

Fig. 1. Plots of M_n (○) and A_2 (●) against w_{Me_2SO} for the glucan A sample in water–Me_2SO mixtures at 25°C.

single chains at $w_{Me_2SO} \sim 0.87$, and that this dissociation was accompanied by an almost discontinuous increase in A_2 [4].

The values of $[\eta]$ and k' of the glucan A sample in water–Me_2SO mixtures at 25°C are summarized in Table 1, and are plotted against w_{Me_2SO} in Fig. 2. The $[\eta]$ value in a mixture of w_{Me_2SO} 0.2 is appreciably larger than that in water, suggesting that the single helix of glucan A in this range is not broken and the chains are more expanded, on account of solvation by the water–Me_2SO mixture. As w_{Me_2SO} increases further from 0.6 to 0.8, the $[\eta]$ values decrease sharply and then approach the values observed in Me_2SO, suggesting that the single helical chains of glucan A change abruptly to semi-flexible chains in this range of w_{Me_2SO}. In addition, up to w_{Me_2SO} 0.2, the k' values decrease sharply and then do not change significantly. Interestingly, k' at $w_{Me_2SO} > 0.4$ approaches the values for a flexible polymer and k' values at w_{Me_2SO} 0.2 are similar to those of triple- or double-helical polysaccharide [6,7]. The changes of k' indicate that the rigidity of the glucan chain decreases with an increase of w_{Me_2SO}. These data show that the solution of glucan A comprises only the intact single helix below w_{Me_2SO} 0.2, with mixtures of single-helix and semi-flexible chains at w_{Me_2SO} between 0.6 and 0.8, and essentially semi-flexible chains at w_{Me_2SO} values of 0.8–1.0.

The values of $[\eta]$ and k' obtained from the glucan A sample in water–diluted Me_2SO are plotted against w_{Me_2SO} in Fig. 3. The $[\eta]$ and k' values in the range of w_{Me_2SO} from 1.0 to 0.4 do not differ appreciably from those in Me_2SO. This result shows that the semi-flexible chains in Me_2SO do not re-form the single helix when the solution is diluted with water to w_{Me_2SO} 0.4. In view of these results, the conformational change of the glucan A in water–Me_2SO is presumed to be an irreversible conversion.

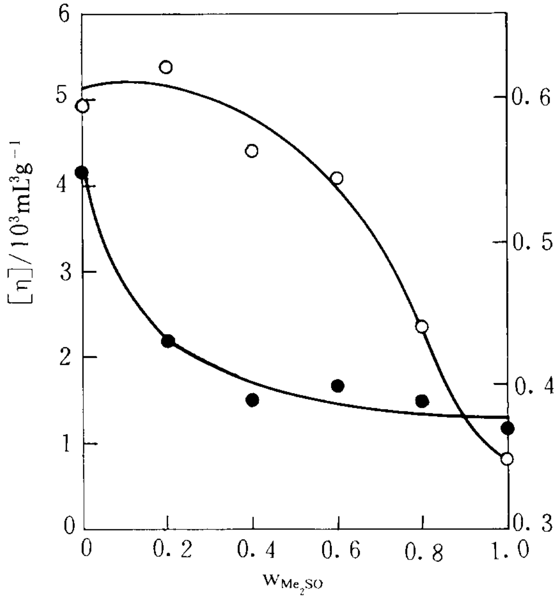

Fig. 2. Plots of [η] (○) and k' (●) against w_{Me_2SO} for glucan A in water–Me_2SO mixtures at 25°C.

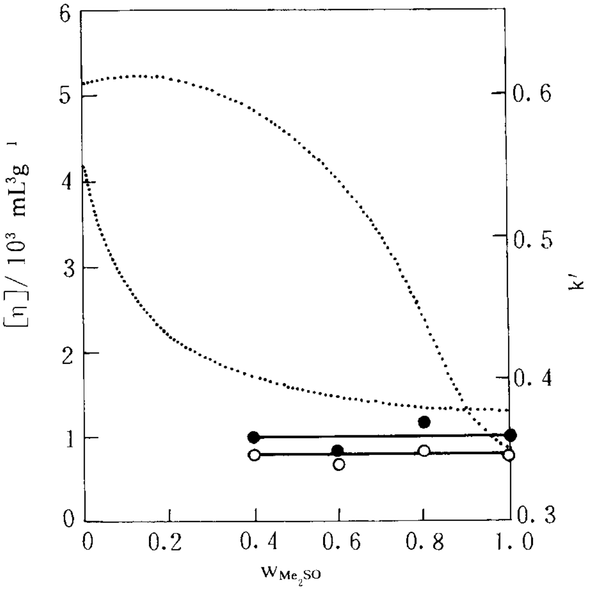

Fig. 3. Composition dependence of [η] (○) and k' (●) for glucan A in water–diluted Me_2SO solution at 25°C. The dotted lines represent the data in Fig. 2.

Straub and Brant [8] reported preferential adsorption in the system of water–Me_2SO and amylose, pullulan, and dextran as determined by gel permeation chromatography (GPC), and they found that all of these glucans preferentially adsorb Me_2SO above w_{Me_2SO} 0.68, a concentration in which the water–Me_2SO mixtures contain an excess of Me_2SO. Interestingly, the $[\eta]$ values of glucan A in water–Me_2SO mixtures decrease sharply in the w_{Me_2SO} range 0.6–0.8 as shown in Fig. 2. Moreover, rotary evaporation of a solution of glucan A in Me_2SO to dryness rendered it insoluble in water. On the basis of these findings, we conjecture that the single-helix chains of glucan A in water–Me_2SO change to semi-flexible chains through breaking of the intramolecular hydrogen bonds that sustain the single helical structure, and this is accompanied by binding of Me_2SO molecules to the glucan chains. The Me_2SO molecules adsorbed on the glucan cannot be desorbed by heating or by dilution with water.

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References

[1] L. Zhang, L. Yang, Q. Ding, and X. Chen, *Carbohydr. Res.*, 270 (1995) 1–10.
[2] L. Zhang and L. Yang, *Biopolymers*, in press.
[3] L. Zhang, A. Hung, and J. Xu, *J. Chem. Chin. Univ.*, 12 (1991) 1126–1129.
[4] T. Sato, T. Norisuye, and H. Fujita, *Macromolecules*, 16 (1983) 185–189.
[5] T. Sato, T. Norisuye, and H. Fujita, *Polym. J.*, 17 (1985) 729–735.
[6] T. Yanaki, T. Norisuye, and H. Fujita, *Macromolecules*, 13 (1980) 1462–1466.
[7] L. Zhang, W. Liu, T. Norisuye, and H. Fujita, *Biopolymers*, 26 (1987) 333–341.
[8] P.R. Straub and D.A. Brant, *Biopolymers*, 19 (1980) 639–653.