THE COMPLEX FORMATION OF CYCLODEXTRINS AND RELATED (1→4)-α-D-GLUCANS AS REVEALED BY THE SPIN LABELING TECHNIQUES

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SUMMARY

The complex formation and inclusion phenomena observed in aqueous solutions of cyclodextrins and some related linear (1→4)-α-D-glucans were investigated furthermore by means of Spin-Label-Induced NMR Relaxation techniques.

A solution of the carbohydrates was incubated with spin labels such as stable nitroxide radicals and paramagnetic metal ions of the lanthanide series. 1H-NMR spectra of these systems indicated that spin labels enhanced the relaxation of the carbohydrate proton nuclei in the vicinity of the binding sites. Remarkable spectral perturbations for cyclodextrins, which may be attributed to the inclusion complex formation, were brought about only when some nitroxide radicals as TEMPO were introduced. This findings were in harmony with the ESR evidence on the matter.
The complex formation phenomena of cyclodextrins and amylose in aqueous solution have drawn the attention of many investigators (1, 2, 3, 4). Various physico-chemical studies, the $^1$H NMR spectroscopic ones in especial demonstrated that the helical nature and the central cavity of these glucans with $\alpha$-$\beta$-$\delta$-(1→4) linkages are responsible for the binding modes and sites in this process, respectively (5-10).

For the aqueous solution of cyclodextrins large $^1$H NMR spectral perturbations are observed with regard to chemical shifts and/or the nuclear magnetic relaxation of resonances by the addition of various dihedral aromatic guest molecules to the systems. The addition of various paramagnetic species as a guest are expected to induce extremely large NMR spectral perturbations (11, 12).

This paper describes an approach to the problem of employing spin-label-induced nuclear magnetic resonance relaxation method (13). This method is a sort of the spin labeling techniques which have been extensively applied in recent years to various biological systems (14-19). Here we have made use of some stable nitroxide radicals and paramagnetic metal ions of the lanthanide series as the spin-label guests. The carbohydrate systems examined were those of $\alpha$-, $\beta$-, $\gamma$-cyclodextrin, some maltooligosaccharides and amyloses of different degree of polymerization.

Materials and Methods

Preparation, identification and physical data of the employed cyclodextrins and nitroxide radicals (TEMPO, TEMPONE, TEMPO; their structures are as follows) were described in our previous literature (19).