Infrared Spectroscopy of Some Mannans

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Infrared absorption spectra for hetero-mannans such as galacto-,¹⁾ gluco-²⁾ and xylo-mannans³⁾ as well as for homo-mannans from yam (*Dioscorea Batas Decne forma Icho*⁴⁾), alga (*Halicoryne wrightii*⁵⁾) and yeast (*Saccharomyces cerevisiae*⁶⁾ and *Candida utilis*⁷⁾) showed two characteristic absorption bands⁸⁾ near 810 and 870 cm^{-1} (Fig. 1), which were not observed for other polysaccharides*; cellulose, xylan and galactan.⁹⁾

FIG. 1. IR-spectrum of the Mannan Obtained from
(A) *Coffea arabica* (Galactomannan)¹⁾
(B) *Amorphophallus konjac* (Glucomannan)²⁾
(C) *Prasiola japonica* (Xylomannan)³⁾
(D) *Halicoryne wrightii* (Mannan)⁴⁾
(E) *Dioscorea Batas Decne forma Icho* (Mannan)⁵⁾
(F) *Saccharomyces cerevisiae* (Mannan)⁶⁾
(G) *Candida utilis* (Mannan)⁷⁾

* Inulin, β -(2 $\rightarrow$ 1) fructan, also shows the bands near 810 and 870 cm^{-1} . However, they are not affected by acetylation.

Since these bands are also observed in the spectra of manno-oligosaccharides which can be regarded as the basic unit of the mannan (Figs. 3 and 4), it is reasonable to consider that they are caused by D-mannose residue in the polymers irrespective of the configuration and position of the mannosidic linkage.

Absorption caused by ring-breathing frequency (type 3) of β -D-mannopyranose occurs at 770 cm^{-1} , whereas that of methyl β -D-mannopyranoside occurs at 795 cm^{-1} .¹⁰⁾ This will be suggestive that the bands near 810 cm^{-1} of the manno-oligosaccharides and mannans are restricted to type 3 absorption of D-mannose residue. In addition, it has been known that acetyl derivative of methyl β -D-mannopyranoside shows type 3 absorption at lower wave-number (747 cm^{-1}) than that of original glycoside (795 cm^{-1}).¹⁰⁾ We observed the similar fact for epichellobiose; the sugar showed the band at 810 cm^{-1} , while the acetate showed at 800 cm^{-1} . Therefore, we may safely say that disappearance of the absorption band near 810 cm^{-1} and concurrent appearance of the band near 775 and 790 cm^{-1} , on acetylation and on methylation of the mannan, respectively, are due to the shift of type 3 absorption band of D-mannose residue (Fig. 2).

It is interesting that the shift of type 3 to high wave-number caused by glycosidation is in contrast to that of D-glucose to low wave-number; the absorption of α -D-glucose series is observed at 774 (α -D-glucose),

FIG. 2. IR-spectrum of the Mannan Derivative.
(A) Acetylated galactomannan (*C. arabica*)
(B) Acetylated glucomannan (*A. konjac*)
(C) Acetylated mannan (*H. wrightii*)
(D) Acetylated xylomannan (*P. japonica*)
(E) Methylated glucomannan (*A. konjac*)

FIG. 3. IR-spectrum of the Manno-oligosaccharide. (A) β -(1 $\rightarrow$ 4) mannosyl glucose (B) β -(1 $\rightarrow$ 4) mannobiosyl glucose (C) mannotriosyl glucose (D) mannotetraosyl glucose (E) α -(1 $\rightarrow$ 6) mannobiosyl glucose

FIG. 4. IR-spectrum of the Manno-oligosaccharide Containing D-Glucose Residue at Reducing End. (A) mannosyl glucose (B) mannobiosyl glucose (C) mannotriosyl glucose (D) mannotetraosyl glucose

745 (methyl α -D-glucopyranoside) and 756 cm^{-1} (amylose), and in α -D-glucose series, at 783 (methyl β -D-glucopyranoside), 773 (cellobiose) and 766 cm^{-1} (cellulose).¹⁰⁾

The absorptions at 860 (for D-mannose) and 880 cm^{-1} (for the acetate) have been assigned to deformation of

equatorial C2-H bond (type 2c),¹⁰⁾ which suggests that the band at 870 cm^{-1} observed in the manno-oligosaccharides and the mannans are also due to type 2c absorption of D-mannose residue. But it is difficult to recognize type 2c absorption of acetyl derivative, because of the presence of intensified type 2b absorption in the near vicinity.

IR-spectrum of yam-mannan is clearly different from that of yeast-mannan in the region 940 to 980 cm^{-1} (Fig. 1). A band near 970 cm^{-1} was observed for not only yeast-mannan but also for manno-oligosaccharides except mannotetraose and the oligosaccharides containing D-glucose residue at the reducing end. This suggests that the bands near 970 cm^{-1} of the oligosaccharides and of yeast-mannan are different in assignment, respectively. On the other hand, a band near 940 cm^{-1} was observed for yam-mannan and for all of the manno-oligosaccharides except α - and β -(1 $\rightarrow$ 6) mannobioses. From these facts, it would be claimed that the absorptions, near 940 and 970 cm^{-1} , are valuable for recognition of the main glycosidic linkage of the mannan.

EXPERIMENTAL

Spectra of the sugars in KBr disk were recorded with a Japan Spectroscopic Co., Ltd., Model IR-S infrared spectrometer. The mannans used were extracted with water (or alkali) and purified *via* the copper-complex. β -(1 $\rightarrow$ 4) Oligosaccharides used are the controlled degradation products of konjac mannan.²⁾ α - and β -(1 $\rightarrow$ 6) Mannobioses are reversion-products of D-mannose by acid.¹¹⁾ The acetyl derivative of the polymer was prepared with acetic anhydride and pyridine in the usual method.¹²⁾

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