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ELECTRON SPIN RESONANCE OF MANGANESE(II) ION IN RAW LEAVES

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Electron spin resonance spectra of manganese(II) ion in some leaves were measured. Spectral pattern of manganese(II) ion in raw leaves was found to be very similar to that of manganese(II) ion in aqueous solutions containing polysaccharides and amino acids.

It has been reported by many authors that manganese(II) ion is necessary for plants and takes part in the decomposition of carbohydrate, the photosynthesis, the activation of enzyme, and so on.[1-4] However, the characterization of manganese-(II) ion in plants still remains open to investigation.

In this study, the electron spin resonance (ESR) spectra of some raw leaves are measured and are compared with the spectra of manganese(II) ion in aqueous solutions containing polysaccharides and amino acids in order to characterize manganese(II) ion in leaves.

ESR spectra were obtained using a JEOL JES FE-3X spectrometer employing 100 kHz modulation and a frequency of 9.1 GHz. Sample temperature was controlled from -50 to -140 °C with a model ES-VT-3A controller and a model ES-UCT-2AX variable temperature accessory. The sample weight of raw leaves is about 100 mg. Solution of manganese(II) ion was made up from manganese(II) aqueous solution (40 mg/l) and excess amount of starch, glucose, L-glutamic acid, methyl alcohol and *n*-butyl alcohol. The volume of the aqueous samples is 0.1 ml. All the samples were put into standard quartz sample tubes of 5 mm outer diameter.

ESR spectra obtained at -100 °C are given in Figs. 1 and 2. Figure 1 shows typical ESR spectra of raw leaves of *Pinus densiflora* (AKAMATSU in Japanese),

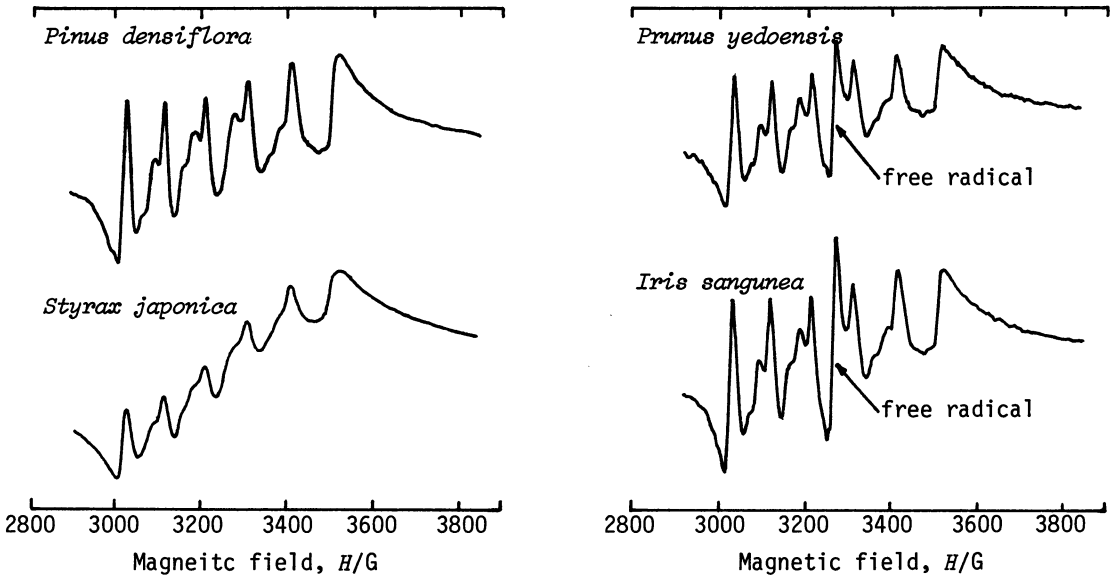

Fig. 1. ESR spectra of raw leaves obtained at -100 °C.

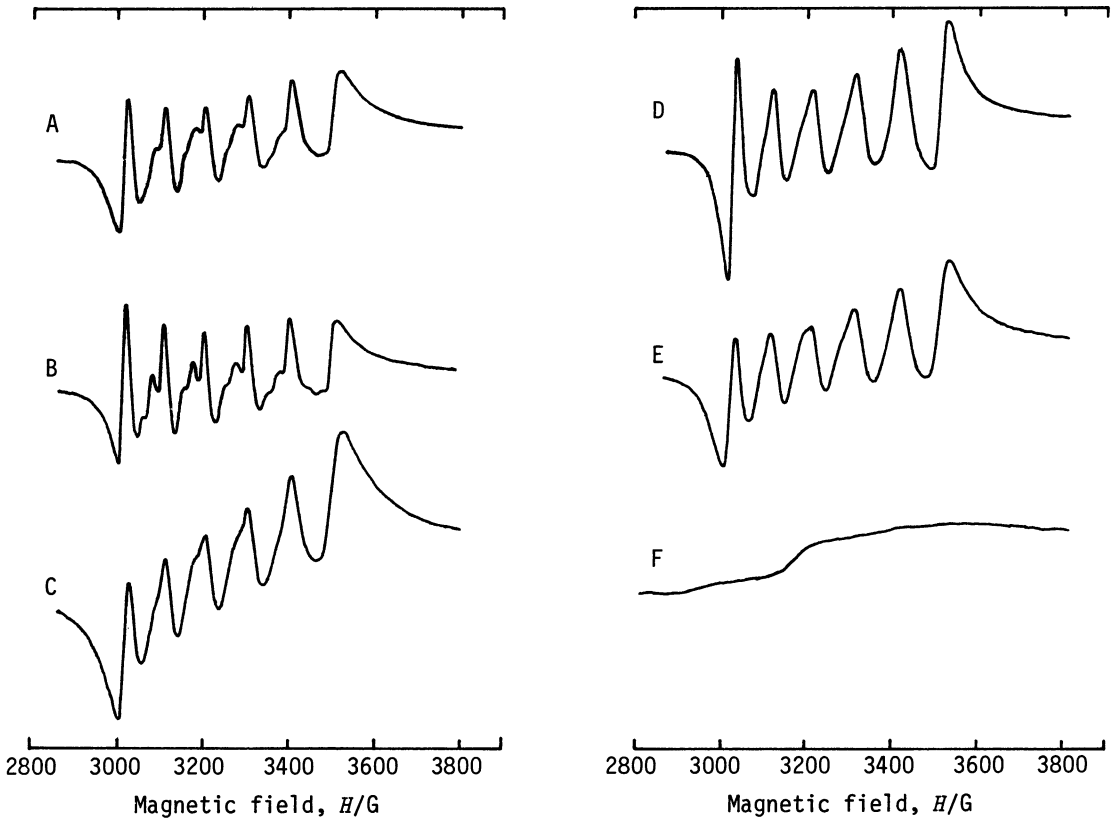

Fig. 2. ESR spectra of aqueous solutions of manganese(II) ion containing (A) starch, (B) glucose, (C) L-glutamic acid, (D) methyl alcohol and (E) *n*-butyl alcohol, and of (F) hexaaquamanganese(II) ion, $[Mn(H_2O)_6]^{2+}$. Temperature is -100 °C.

Styrax japonica (EGONOKI), *Prunus yedoensis* (SOMEI YOSHINO), and *Iris sangunea* (AYAME). All the spectra indicate normal six hyperfine structures (hfs) of manganese(II) with small forbidden signals. For last two leaves, the signal of free radical appears arround 3250 G (≡ 10^{-4} T) in the ESR spectra. Figure 2 shows ESR spectra of manganese(II) ion in the aqueous solutions containing starch, glucose, L-glutamic acid, methyl alcohol, and *n*-butyl alcohol. In Fig. 2, spectrum of hexaaquamanganese(II) ion, $[Mn(H_2O)_6]^{2+}$, is also given. Although the ESR spectrum of hexaaquamanganese(II) ion was broad and not well-defined, the other aqueous samples gave six clear hfs of manganese(II) ion. These results, therefore, suggest that manganese(II) ion in raw leaves interacts with the compounds containing OH-group and amino acid.

When the ESR spectra in Figs. 1 and 2 are compared, the spectral pattern of leaves and the aqueous samples containing starch, glucose and L-glutamic acid shows

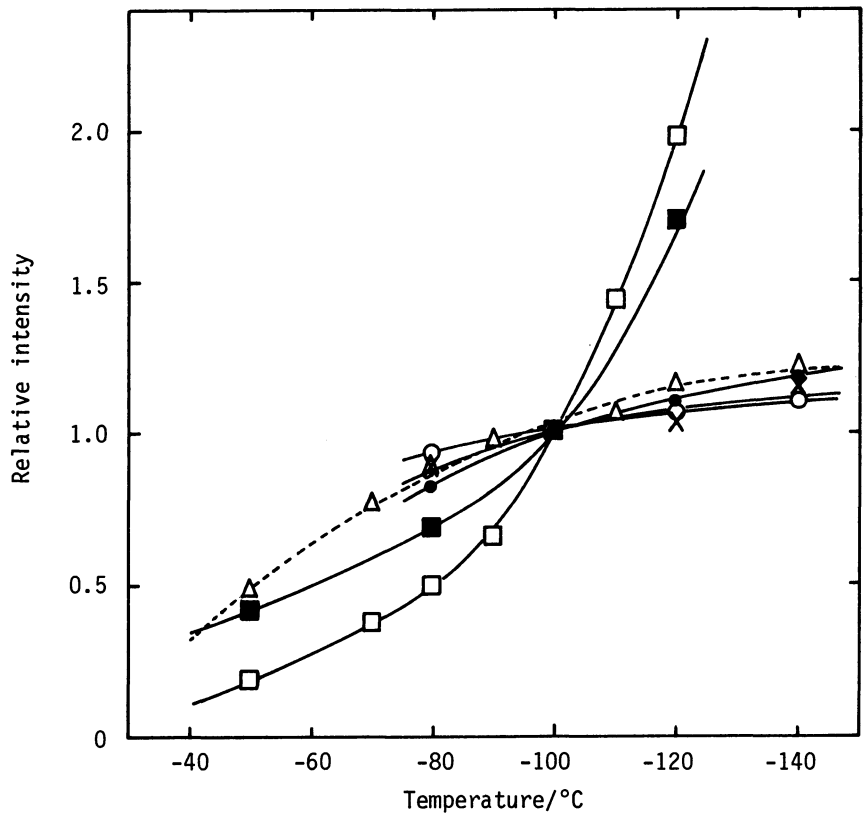

Fig. 3. The plot of relative intensity of first signal of manganese(II) ion at low magnetic field *vs.* temperature. The samples are leaves of *Pinus densiflora* (△) and aqueous solutions of manganese(II) ion containing methyl alcohol (□), *n*-butyl alcohol (■), starch (○), glucose (●) and L-glutamic acid (X).

good similarities. Especially, ESR spectra of manganese(II) ion in *Pinus densiflora*, *Prunus yedoensis* and *Iris sangunea* are very similar to those of aqueous samples containing starch and glucose.

Such similarities are also observed from the temperature dependence of signal intensity of the first hfs at low magnetic field. The relative intensity, that is, the ratio of this signal intensity at various temperature to that at -100 °C, is calculated and plotted against the temperature in Fig. 3. The temperature dependence of *Pinus densiflora* as an example of leaves is found to agree with that of the aqueous samples containing starch, glucose and L-glutamic acid. Although methyl alcohol and *n*-butyl alcohol have an OH-group, the behavior of their solutions is different from raw leaves. From the results, it is supposed that manganese(II) ion in raw leaves exists in the form interacting with polysaccharide and/or amino acid.

Finally, the characterization of manganese(II) ion in leaves is now being investigated in more detail by the ESR measurements using many kinds of polysaccharides, amino acids and proteins.

References

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