Structure of Malonogalactan :
Carbon-13 Nuclear Magnetic
Resonance Spectra of
Malonogalactan

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In previous papers,^{1,2)} it was shown that the malonogalactan obtained from *Penicillium citrinum* Thom 1131 was a 1,5- β -galactofuranoside polymer esterified with malonic acid at the C-2 or C-3 position and consisted of D-galactose and malonic acid in the approximate molar ratio of 3:1. In this note, the configuration of the malonogalactan is further elucidated by ¹³C NMR spectrometry, and it is concluded that the galactofuranoside polymer was esterified with malonic acid at the C-3 position. ¹³C NMR spectra were obtained on a Hitachi R-26 spectrometer operating in the Fourier transform mode at 10.0 MHz.

The proton noise-decoupled ¹³C NMR spectra of the malonogalactan and the galactan (demalonylated malonogalactan) in D₂O shows that they were homogeneous polysaccharides (Fig. 1). In the ¹³C NMR spectrum of the galactan (Fig. 1A), the peak at 108 ppm for the anomeric carbon seems to correspond to the peak of the C-1 carbon of 1,2-*trans* furanosides, because, T. Usui *et al.*³⁾ recently proposed that the peak of the C-1 carbon of the 1,2-*trans* methyl furanosides (about 109 ppm) shifted downfield by 5~6 ppm from that of the 1,2-*cis* methyl furanosides (about 104 ppm). Therefore the anomeric carbons are confirmed to be involved in β -linkage. The peak of the C-5 carbons of furanosides was reported to appear at 60~65 ppm.^{3~6)} So the peak of the C-5 carbon of the β -galactofuranoside should appear at 68~72 ppm. In the *Penicillium* galactan, however, the peak of the C-5 carbon was found to shift downfield to 77.5 or 78 ppm. This fact suggests that the C-5 carbons were involved in the glycosidic linkage. Thus, the galactan is concluded to contain exclusively β 1-5 linkages. This conclusion coincides with the result in our previous paper.²⁾

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FIG. 1. C-13 NMR Spectra of the Galactan (A) and Malonogalactan (B).

The other carbons were assigned in comparison with the methyl α -L-arabinofuranoside.³⁾ The peaks at 62.5 and either of 77.5 and 78 ppm could be assigned to the C-6 and C-3 carbons, respectively. The peak at 83 ppm had an increased intensity and could be assigned to the overlapped peaks of the C-2 and C-4 carbons. In the ¹³C NMR spectrum of the malonogalactan (Fig. 1B), the peaks of the galactose moiety were identical with those of the galactan.

We reported already that the malonogalactan was esterified with malonic acid at C-2 or C-3 position.²⁾ If the esterified position were C-2, the peak of the C-2 carbon should be observed in the lower field than that of the galactan. However, such shift was not observed in the ¹³C NMR spectrum of the malonogalactan (Fig. 1B). So the esterified position was concluded to be C-3. The peak of the C-3 carbon bonded to the esterified oxygen shifted to 83 ppm from 77.5 ppm and it was overlapped with the peaks of the C-2 and C-4 carbons. The peak of 77.5 ppm in the malonogalactan was smaller than that in the galactan, so it seems reasonable to assign the peaks of 77.5 and 78 ppm to the C-3 and C-5 carbons, respectively.

In the ¹³C NMR spectrum of the malonogalactan, 4 peaks (66, 76, 171.5 and 174 ppm) due to the carbons of the malonic acid moiety were recognized. Among them, the peaks at 171.5 and 174 ppm could be assigned to the ester-carboxyl carbon and the free carboxyl carbon, respectively.⁴⁾ The signal intensity of the peak at 171.5 ppm (the ester-carboxyl carbon) was much stronger than the peak at 174 ppm (the free carboxyl carbon). Thus, there is a possibility that some of the

TABLE I. CARBON-13 CHEMICAL SHIFTS^{a)}

	1-Methyl α - L-arabino- furanoside ^{b)}	Malono- galactan	Galactan
C-1	109.5	108	108
C-2	82.0	83	83
C-3	77.9	83 and 77.5	77.5
C-4	84.8	83	83
C-5	62.5	78	78
C-6	—	62.5	62.5
Ester-carboxyl C	—	171.5	—
Methylene C	—	66 and 76	—
Free carboxyl C	—	174	—

^{a)} In ppm downfield from external TMS.^{b)} T. Usui *et al.* *Agr. Biol. Chem.*, **38**, 1409(1974).

malonic acid residues have the diester linkage in the malonogalactan, although it is generally dangerous to compare the signal intensity of peaks in proton noise-decoupled FT ¹³C NMR spectra. If this possibility is correct, the remaining peaks at 66 and 76 ppm would be assigned to the methylene carbon of the malonic acid monoester and that of the diester, respectively. The methylene signal of free malonic acid appears at 41 ppm and the α -carbon signal of ester usually appears somewhat upper field than that of free acid.⁴⁾ Those peaks at 66 and 76 ppm appear at extremely low field as the α -carbon signal and can be assumed to have the average chemical-shifts of the high-speed tautomerism of keto-

enol ($sp^3 \rightleftharpoons sp^2$). Hence, there should be two kinds of malonic residue in the malonogalactan, and the peak at 76 ppm would be assigned in the malonic acid diester, as the enol type is assumed to be more predominant in the diester than in the monoester. Probably, the resulted diester bridges would not be intermolecular but intramolecular, because the malonogalactan is very soluble in water (> 500 mg/ml).

On the basis of the ¹³C NMR spectra, whose chemical shifts are summarized in Table I, the malonogalactan is concluded to be a polysaccharide that has β 1 $\rightarrow$ 5 linkage and is esterified with malonic acid at the position of 3.

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