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^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA OF GLUCOBIOSES

Naotaka Yamaoka, Taichi Usui, Kazuo Matsuda and Katura Tuzimura
Faculty of Agriculture, Tohoku University, Tsutsumidori Amamiya-machi, Sendai, Japan.
Hiroshi Sugiyama and Shuichi Seto
Chemical Research Institute of Non-Aqueous Solution, Tohoku University, Katahiracho, Sendai, Japan.

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WE report some preliminary studies of configuration of various glucobioses by ^{13}C NMR. The utility of PMR spectroscopy for establishing of configuration of glucobioses (H-1) in solution has been deduced by the application of the Karplus relationship.[1] However, the anomeric proton signals of glucobioses are heavily overlapped with other protons. Studies of the ^{13}C NMR spectra of monosaccharides were published by other groups,[2,3] but the utility of ^{13}C NMR for the assignment of the configuration of glycosidic linkage (C-1') in a disaccharide has not been published. Data on the C-1 resonance of α and β anomers in methyl D-glucopyranoside[2] could be used in the conjunction with relative peak heights to distinguish the constitution of the glycosidic linked carbon.

The C-1 resonance of the anomeric carbon of D-glucose was shifted downfield by methylation of the anomeric hydroxyl group.[2] The comparison of the C-1' resonance of α-linked glucobioses with α-D-glucopyranose showed that the linked carbon resonance was shifted downfield by 4.4~8.1 ppm by O-glucosylation of the α-hydroxyl group. Also, the comparison of the β-linked glucobioses with β-D-glucopyranose showed that the linked carbon resonance was shifted downfield by 7.0~8.5 ppm by O-glucosylation of the β-anomeric hydroxyl group. These criteria allow straightforward assignment of the C-1' resonance of glucobioses (see the TABLE 1). The ^{13}C NMR spectral data on glucobioses could be used to distinguish the C-1' resonance of the α and β linked carbon in all cases as shown in the

TABLE 1

^{13}C-1' Chemical shifts for glucobioses

Derivatives		Chemical shifts[a)]
Methyl α-D-glucopyranoside		93.4[2)]
Kojibiose	(1,2-α)	96.1
Nigerose	(1,3-α)	93.4
Maltose	(1,4-α)	92.4
Methyl β-D-glucopyranoside		89.3[2)]
Sophorose	(1,2-β)	88.2
Laminaribiose	(1,3-β)	89.7
Cellobiose	(1,4-β)	89.7

a) In ppm upfield from external $^{13}CS_2$; in H_2O.

TABLE 1. However, the C-1' signal of kojibiose appeared at a higher field by 3 ppm than the other glucobioses examined.

The ^{13}C NMR spectrum of laminaribiose clearly showed the configuration of the linked anomeric carbon (C-1') and two kinds of anomeric carbons (C-1), and furthermore the verification of ^{13}C NMR assignment of laminaribiose was available from the comparison of its spectrum with that of 3-O-methyl-α (or β)-D-glucopyranose,[2)] as shown in the FIGURE 1.

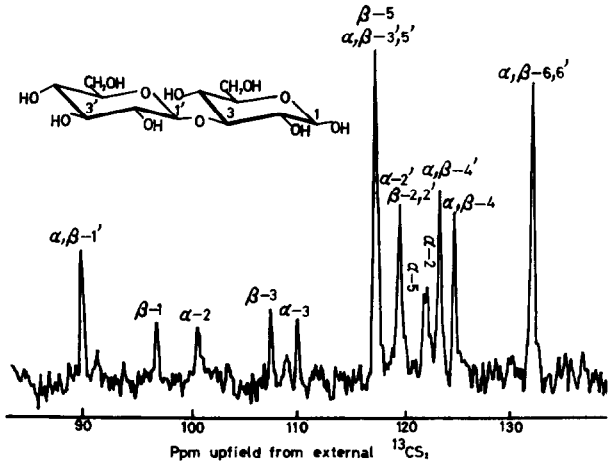

Fig. 1. The proton noise-decoupled, natural-abundance ^{13}C NMR spectrum of the anomeric mixture of laminaribiose in H_2O at 25 MHz; time-averaging 256 scans.

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