Determination of Anomeric Configuration of Furanoside Derivatives by Carbon-13 NMR

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Our previous work on gluco-oligosaccharides and glucans showed that C-13 NMR spectroscopy was a useful tool for the determination of the structural feature of the glycosidic bond.¹⁾ The proton-noise-decoupled C-13 pulse Fourier transform (FT) spectrum demonstrates remarkable resolution and scope for studies of polysaccharides.^{1,2)} This report describes that C-13 NMR is also useful for the determination of the anomeric configuration of the furanosyl residue in neomycin C

and arabinogalactan, although the former has been obtained from proton NMR spectral studies.³⁾ However, for the proton NMR spectra in deuterium oxide of methyl furanosides,⁴⁾ it has been reported that assignments of anomeric configuration could not be made on the basis of the chemical shifts of H-1 and methyl signals, and both α - and β -anomers of methyl furanosides showed very close $J_{1,2}$ coupling constants. This was confirmed in our study with methyl D-ribofuranosides and methyl L-arabinofuranosides as shown in Table I.

On the other hand, the C-13 spectra can be recognized from Table II for the determination of the anomeric configuration of methyl furanosides. That is, the C-1 resonance of the 1,2-*trans* compound (2 and 3) shifts downfield about 5~6 ppm from that of the 1,2-*cis* compound (1 and 4). It should be noted that the resonance of the anomeric carbon in methyl furanosides appears at the lower field than in the corresponding methyl pyranosides.⁵⁾ The other carbon assignment is based on the assignment of the earlier studies⁶⁾ for ribonucleosides. The anomeric change from *trans* to *cis* form of 1,2-arrangement affects upfield on C-2 by 1,2-eclipse interaction.

TABLE I. PROTON CHEMICAL SHIFTS^{a)} OF METHYL-FURANOSIDES

	δ	$J_{1,2}$ -value	O-CH ₃
(1) Methyl α -D-ribofuranoside	5.04	2.0	3.42
(2) Methyl β -D-ribofuranoside	4.94	1.0<	3.40
(3) Methyl α -L-arabinofuranoside	4.98	3.3	3.39
(4) Methyl β -L-arabinofuranoside	4.88	1.0<	3.39

^{a)} In ppm downfield from internal DSS. All spectra were measured at room temperature at 90 MHz in deuterium oxide, by using Hitachi R-22 spectrometer.

TABLE II. CARBON-13 CHEMICAL SHIFTS^{b)} OF METHYL-FURANOSIDES

	C-1	C-2	C-3	C-4	C-5	O-CH ₃
(1) Methyl α -D-ribofuranoside	104.3	72.5	72.3	83.7	63.0	56.4
(2) Methyl β -D-ribofuranoside	109.2	75.6	71.0	85.8	64.4	56.4
(3) Methyl α -L-arabinofuranoside	109.5	82.0	77.9	84.8	62.5	55.6
(4) Methyl β -L-arabinofuranoside	103.3	76.3	77.9	83.1	64.3	56.1

^{b)} In ppm downfield from external TMS.
C-13 NMR spectra were measured at 22.6 MHz by R-22 FT spectrometer.
Internal D lock.

This shows the characteristic pattern of the furanoside form.

The chemical shift of the anomeric carbon in methyl furanosides is expected to correspond to that of the furanoside residue in neomycin C and arabinogalactan. We have already reported that the shieldings of the glycosidic carbon (C-1') in a series of α - and β -glucobioses correspond to the C-1 resonance of α - and β -anomers in methyl D-glucopyranoside.⁷⁾ The stereochemistry of the ribose-neamine linkage in neomycin C was clearly established by C-13 NMR spectroscopy. The C-13 NMR of neomycin C in deuterium oxide showed two peaks at 110.3 and 96.4 ppm for anomeric carbons. The intensity of the latter was about twice as much as that of the former. The peak at 110.3 ppm could be readily assigned to the β -anomeric carbon of the ribofuranoside linkage by comparison with methyl D-ribofuranoside. The latter corresponded to two α -anomeric carbons of the 2,6-diamino-2,6-dideoxy D-glucopyranoside linkage (neosamine C). The spectrum of an arabinogalactan isolated from green coffee bean was studied. This galactan has been reported by Wolfrom *et al.*,⁸⁾ which has a backbone chain composed of β -D-(1-3) and β -D-(1-6) linked galactopyranosyl residues. L-Arabinofuranosyl residues are attached at the C-3 and C-6 position of the galactopyranosyl residues as the most prevalent side chain.

The anomeric configuration of arabinofuranosyl residues is not yet known. By comparing with the methyl L-arabinofuranosides arabinofuranosyl residues in the arabinogalactan were shown to have α -configuration as follows. The C-13 and proton NMR of this compound were measured in deuterium oxide. C-13 NMR showed four peaks due to anomeric carbons between 112.4 and 104.0 ppm as shown in the Fig. Apparently, the chemical shifts of peaks 3 and 4 were respectively assigned to the β -D-(1-3) and β -D-(1-6) anomeric carbons of galactopyranosyl residues, considering the results of earlier studies.^{1,9)} The chemical shifts of both peaks

FIG. 1. Proton-noise-decoupled Pulse C-13 NMR Spectrum of Arabinogalactan in Anomeric Region.

Spectrum was measured at room temperature at 22.6 MHz with the Hitachi R-22 pulse FT system. External ^{19}F lock. Peak at 108 ppm was a noise.

1 and 2 provide reasonable approximation to the anomeric carbon of methyl α -L-arabinofuranoside. This interpretation is also supported by relative intensities of anomeric protons by proton NMR.¹⁰⁾ The assignment of these peaks will be reported in detail in near future.

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