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Carbon-13 Nuclear Magnetic Resonance Spectra of α-Ribonucleosides

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Synopsis. The C-13 NMR spectra of four α- and two β-ribonucleosides have been measured and all carbon signals have been assigned.

Although a naturally occuring α-ribonucleoside is found only as a part of vitamine B_{12},[1] there is a great possibility to find α-ribonucleosides which are highly biologically active like vitamine B_{12}. Carbon-13 NMR spectroscopy is a useful tool for the investigation of biologically important substances because of large chemical shift differences and susceptibilities to conformational and configurational changes.[2] The present authors have shown its application to oligosaccharides and glucans.[3,4] At the present time, its application to α-ribonucleosides has been intended.

Carbon-13 NMR studies of β-ribonucleosides and nucleotides have been published by Dorman and Roberts[5] and Jones *et al.*[6] Recently, Mantsch and Smith have indicated the reverse assignment of C-13 signals due to C-2′ and C-3′.[7] Our assignment of C-13 signals in the spectra of α-ribonucleosides was based on a comparison with those studies. As shown in the Table, the signals due to carbons of the sugar moiety appear between δ 90 and 60 ppm and those of the base moiety do between δ 160 and 130 ppm except the methyl signals. The C-2′ and C-3′ signal assignments for the β-anomers by Dorman[5] and Jones[6] are reversed to those given in the Table. The present assignment is based on the sterical reason as follows. The anomeric change from α to β should afford a more marked effect on the C-2′ chemical shift than on the C-3′ chemical shift, and the C-2′ and C-3′ signals of the α-anomers appear at the same field strength. Therefore, the signal which shows a downfield shift should be assigned to C-2′ of the β-anomers. As a result, the signal at δ 74 ppm is attributed to C-2′, and the assignment by Mantsch and Smith seems more reasonable. The C-3′ and C-5′ signals of both anomers appear at the same field strength. The C-4′ signals of the α-anomers appear at a little lower field than those of the β-anomers except that of theophylline.

Carbons in the base moieties of the purine-α- and -β-ribosides show almost the same chemical shifts, but those of the pyrimidine-α- and -β-ribosides show little different chemical-shifts as seen from the Table. Jones *et al.* showed that the chemical shifts for a base moiety change according to the *syn* and the *anti* conformation of the C–N riboside bond.[8] Hence, the distribution of the rotamer of the purine ribosides on the riboside bond is the same in the both α- and β-anomers.[9] In the case of the pyrimidine ribosides, that is different between α- and β-anomers. Since *N*-acetylproline shows the higher Cα chemical shift in the *trans*-rotamer than in the *cis*-rotamer,[10] the signal at δ 27.6 ppm in the spectra of (IIα and β) can be assigned to N_1–Me and that at δ 29 ppm to N_3–Me. In the case of (IIβ), the C-3′, C-4′, and N_3–Me signals are shifted to higher fields than those of (IIa). This fact can be explained by the reason that N_3–Me of the *syn* rotamer comes over on C-3′ and C-4′ and interacts sterically with those atoms.

Experimental

Materials. The all α-ribosides[11] and theophylline[12] and thymine β-ribosides[13] were synthesized as reported before. Adenine and uracil β-ribosides were purchased from Seikagaku Kogyo.

Measurement of C-13 NMR Spectra. The spectra were measured with a JEOL PFT-100 spectrometer and an EC-6 computer at 25.15 MHz. Deuterium internal-lock on a solvent was used. Pulse width and repetition time were

TABLE 1. C-13 CHEMICAL SHIFTS OF α- AND β-RIBONUCLEOSIDES

		Me	C-2	C-4	C-5	C-6	C-8	C-1′	C-2′	C-3′	C-4′	C-5′
I	α		153.2	150.4	119.1	156.7	142.7	86.1	71.8	71.8	84.9	62.6
	β		153.4	149.9	120.3	157.1	141.1	89.0	74.6	71.7	86.9	62.7
II	α	27.6 29.6	151.0	148.0	105.9	154.5	142.3	66.7	71.2	70.6	85.1	61.3
	β	27.6 29.4	150.7	149.3	105.4	154.0	142.0	87.7	73.1	69.5	79.4	62.7
III	α		150.6	163.5	99.8	142.9		85.2	70.6	70.6	84.2	61.3
	β		152.4	164.7	103.1	142.2		89.1	74.9	71.1	86.0	62.2
IV	α	12.6	150.9	164.5	107.6	139.9		85.5	70.8	70.8	84.2	61.6
	β	12.1	150.9	164.4	109.7	137.7		87.3	73.8	70.2	85.0	61.5

δ_C (ppm downfield from TMS) which is converted using the factor of $\delta_C^{d_6\text{-DMSO}}$ 39.5 ppm.
I; adenine-riboside, II; theorphylline-ribosides, III: uracil-riboside, IV; thymine-riboside.

13 μs ($\pi/4$ pulse) and 2 s, respectively. All protons were decoupled by the noise modulation method with 30 W power. The material concentrations were 10—20 mg in 0.2 ml of d_6-dimethyl sulfoxide.

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