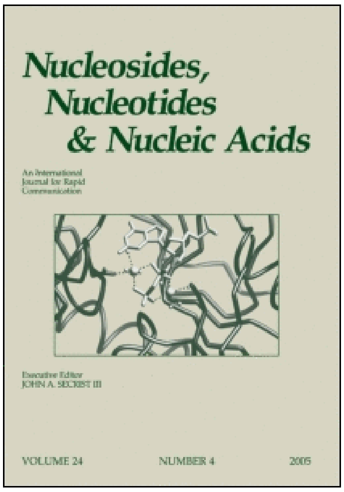

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ASSIGNMENT OF ^{13}C CHEMICAL SHIFTS OF α-D-RIBONUCLEOSIDE SUGAR CARBONS BY $^{1}J(CH)$ COUPLING CONSTANTS

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ABSTRACT: The $^{1}J(CH)$ coupling constant of C-1' in nucleosides is increased compared to those of the other carbons of the sugar moiety. Applying this to several D-ribonucleosides the signals C-4'/C-1' of these α-anomers are reversed to those of the β-counterparts (C-1'/C-4'). This phenomenon and the broadening of the C-3' signal compared to that of C-2' establishes the sequence C-4', 1', 2', 3', 5' (increasing field) for a number of α-D-ribonucleosides.

The constituents of ribonucleic acids, the common D-ribonucleosides as well as their rare analogues[1,2] are exclusively β-configurated at the anomeric center. However, as a result of nonstereospecific chemical glycosylation α-D-nucleosides are formed under certain conditions[3]. Some of them exhibit extraordinary biological activity and are inhibitors of enzymes[4]. Finally an α-D-ribonucleoside is an integral part of vitamine B_{12}[5].

Since ^{13}C NMR spectroscopy became an important method for the elucidation of nucleic acid constituents the assignment of the ^{13}C chemical shifts of the sugar moiety was established in the series of the β-anomers[6]. Not much attention has been paid to the α-counterparts and until recently our assignments were based on a report by Sugiyama[7].

RESULTS AND DISCUSSION

According to previous results[7] the chemical shifts of α-D-ribonucleosides were ordered in the sequence C-1',4',2',3',5' with decreasing

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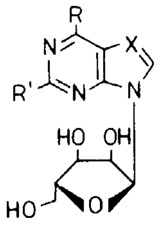
δ-values. Inspecting the ^{13}C NMR data of α-D-arabinonucleosides, which have been assigned by exchange of the sugar protons by deuterium[8], we noticed that the C-4' as well as the C-5'-signals of both anomers show almost the same shielding[9] whereas the chemical shifts of C-1' differ by about 5 ppm. If one agrees that the C-4' and C-5' chemical shifts are not much influenced by substitution at C-1' the chemical shift of C-1' and C-4' of α-D-ribonucleosides should be reversed compared to the β-anomers. This sequence is then in contrast to previous results[7].

To solve this problem the ^{1}J(CH)coupling constants of the sugar carbons of α- and β-D-ribonucleosides, such as 1a-c and 2a-c, have been measured.



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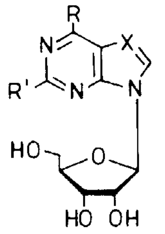

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	X	R	R'
a	N	NH_2	H
b	CH	NH_2	H
c	CH	Cl	SCH_3

The table shows that four coupling constants exhibit values around 140-150 Hz whereas one coupling constant is definitely increased by more than 10 Hz. Since ^{1}J(CH)coupling constants of carbons increase with the electronegativity of its ligands[6] the larger coupling constant of the anomers of adenosine (1a/2a) or tubercidin (1b/2b) have to be assigned to the signal of C-1'. Applying this to α-D-ribonucleosides C-4' is located at the lowest field followed by C-1'.

As the table demonstrates the large coupling constant of C-1' is very similar in purine and 7-deazapurine nucleosides and this phenomenon may be generalized for nucleosides having a N-glycosylic bond.

By using the sequence of C-4',C-1' for α-D-ribonucleosides and keeping in mind that C-5' shows a triplet of the CH-coupling, only the signals of C-2' and C-3' were left to be assigned. As can be seen from the table C-2' and C-3' of α-D-ribonucleosides may coincide. If the signals are separated one of them shows a larger line width than the other. As C-3' exhibits the most complex coupling pattern, due to several ^{3}J(CH)

Table. Chemical shifts[a] and ^1J(CH)coupling constants of the anomers of adenosine, tubercidin and the synthetic precursors 1c/2c.

Compd	C-1'	C-2'	C-3'	C-4'	C-5'
1a	83.3 (d,165)	70.5 (d,148)	70.5 (d,150)[c]	84.7 (d,150)	61.3 (t,140)
2a[b]	88.5 (d,165)	74.3 (d,146)	70.3 (d,150)	85.6 (d,150)	61.3 (t,140)
1b	83.4 (d,162)	70.9 (d,150)	70.7[c](d,146)	83.9 (d,146)	61.6 (t,139)
2b	87.6 (d,163)	73.7 (d,147)	70.8 (d,151)	85.1 (d,149)	61.9 (t,142)
1c	84.0 (d,164)	70.9 (d,150)	70.7[c](d,147)	85.0 (d,147)	61.6 (t,139)
2c	87.3 (d,164)	74.1 (d,149)	70.5 (d,146)	85.3 (d,147)	61.6 (t,135)

[a] Chemical shifts in ppm relative to TMS; coupling constants in Hz; [b] data taken from ref.[11]; [c] broader signals compared to C-2'.

couplings the broader signal has to be assigned to this carbon. As a consequence C-2' is located downfield from C-3'.

In conclusion the large ^1J(CH)coupling constant of the anomeric carbons of nucleosides having a N-glycosylic bond allows a fast identification of this carbon without refering to time consuming decoupling experiments. As a consequence C-4' is located downfield to C-1' in a number of α-D-ribonucleosides which were subject to this investigation.

EXPERIMENTAL

Purine nucleosides have been purchased from Sigma Chemie GmbH, Taufkirchen, Germany; 7-deazapurine nucleosides have been synthesized in our laboratory and methods are available from reference[10]. Natural abundance FT ^{13}C NMR spectra were obtained at ambient temperature on a Bruker WM-250 spectrometer operating at 62.896 MHz. Typical condition were: memory size, 16 K; pulse width 30°; relaxation delay 5 s; digital resolution 1 Hz. Samples were run in nearly saturated Me_2SO-d_6/D_2O (1:1) solution.

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