USE OF BROADENED ^{13}C NMR SIGNALS IN COMPLEXES OF NUCLEOSIDES WITH Mn(II) TO EVALUATE THE CONFORMATIONAL EQUILIBRIUM OF THE RIBOSE RING

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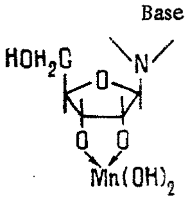
The ^{13}C NMR spectra of chelate complexes of nucleosides with Mn(II) under fast-exchange conditions have been studied. It has been established that the state of the conformational equilibrium of the ribose ring within the framework of the two-sided exchange 2'-endo (S) ⇄ 3'-endo (N) can easily be evaluated from the broadening of the C-1' and C-4' signals. The results obtained by the broadening method agree well with those of methods used previously.

We have previously [1] established the formation of chelate complexes (I) of nucleosides with Mn(II) and have shown the possibility of their use for determining the comformations of nucleosides since it is known [2] that the broadening of NMR signals depends greatly on the distance r to the paramagnetic ion. In the course of further investigations it has been found that the state of the conformational equilibrium of the ribose ring within the framework of the two-sided exchange 2'-endo (S) ⇄ 3'-endo (N) can easily be evaluated from the broadening of the C-1' and C-4' signals in complexes of nucleosides with Mn(II). Their maximum broadening is observed in the 2'-endo (S) and 3'-endo (N) conformations, respectively (Fig. 1). In view of the existence of the conjugations of rapid exchange, broadening at a constant concentration of Mn(II) depends only on the conformational equilibrium:



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$$P_1\Delta_1 + P_2\Delta_2 = \Delta\nu^{obs}_{1'}, \quad (1)$$

$$P_1\Delta_2 + P_2\Delta_1 = \Delta\nu^{obs}_{4'}, \quad (2)$$

$$P_1 + P_2 = 1, \quad (3)$$

where

Δ_1 is the broadening of the C-1' signal in the 2'-endo (S) conformation and of the C-4' signal in the 3'-endo (N) conformation (the same from symmetry considerations) at a concentration of Mn(II);

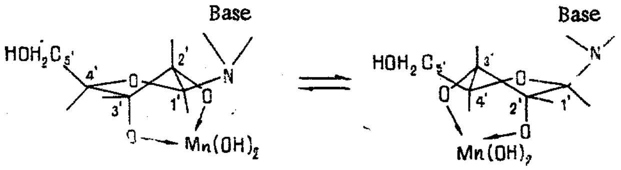

Fig. 1. The two-sided exchange 2'-endo ⇄ 3'-endo in complexes of nucleosides with Mn(II).

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Δ_2 is the broadening of the C-1' signal in the 3'-endo (N) and of the C-4' signal in the 2'-endo (S) conformation (identical from symmetry considerations) at a constant concentration of Mn(II);

$\Delta\nu_{1'}^{obs}$ and $\Delta\nu_{4'}^{obs}$ are the observed broadenings of the C-1' and C-4' signals, respectively, at a constant concentration of Mn(II); and

P_1 and P_2 are the populations of the 2'-endo (S) and 3'-endo (N) conformations (in molar fractions), respectively.

In view of the fact the $\Delta_2 \ll \Delta_1$ (since the broadening is proportional to r^6), it is possible to adopt the approximation $\Delta_2 = 0$. Then

$$P_1 = \frac{\Delta\nu_{1'}^{obs}}{\Delta\nu_{1'}^{obs} + \Delta\nu_{4'}^{obs}}, \tag{4}$$

and

$$P_2 = \frac{\Delta\nu_{4'}^{obs}}{\Delta\nu_{1'}^{obs} + \Delta\nu_{4'}^{obs}}. \tag{5}$$

It can be shown that under the conditions $\Delta\nu_{1'}^{obs} = \Delta\nu_{4'}^{obs}$ the populations of the conformations are the same ($P_1 = P_2 = 0.5$) do not depend on the absolute values of Δ_1 and Δ_2 or, consequently, on the approximation $\Delta_2 = 0$. This makes it possible to evaluate the conformational equilibrium of the ribose ring within the framework of the two-sided exchange 2'-endo (S) $\rightleftarrows$ 3'-endo (N) with the accuracy of the error of measurement, provided that the difference in the populations is only slight. Preliminary measurements have shown that the results obtained by the broadening method agree well with those of methods used previously [3, 4]:

Nucleoside	Method [3]	Method [4]	Broadening method
Cytidine	40±10%	44±10%	45±3%
Uridine	48	54	52
Adenosine	60	70	76±6%

The latter [3, 4] were based on a determination of the torsional angles of the ribose ring and their use to interpret the spin-spin coupling constants of the protons. According to Lee et al. [5], the error of the method amounts ±10%.

The ^{13}C NMR spectra were taken on a WH-90 spectrometer with a frequency of 22.63 MHz at a temperature of 30±1°C. The broadenings were measured with an accuracy of ±0.3 Hz.

SUMMARY

It has been established that the conformational equilibrium in nucleosides can be evaluated from the broadening of the C-1' and C-4'signals in their complexes with Mn(II).

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