^{13}C-NMR SPECTRA OF ALDOSES IN MOLYBDATE COMPLEXES*

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Analysis of ^{13}C-NMR spectra has shown that ribose, talose and allose behave as trident donors in their molybdate complexes using hydroxyl groups at $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$, whereas lyxose and mannose use the hydroxyl groups at $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$.

In our previous paper[1] it was shown by analysis of ^{1}H-NMR spectra that aldoses of the homomorphous series of lyxose (D-lyxose, D-mannose and D-*glycero*-L-*manno*-heptose, D-*glycero*-D-*gulo*-heptose) in their molybdate complexes assume pyranoid structures in conformations close to $^1S_5$ and $^5S_1$, respectively, *i.e.* with the hydroxyl groups arranged as $1a - 2e - 3q$. Aldoses of the homomorphous series of ribose (L-ribose, D-talose, D-*glycero*-D-*talo*-heptose) in molybdate complexes produced ^{1}H-NMR spectra with broad overlapping signals which could not be analyzed. For further information about molybdate complexes of aldoses of the homomorphous series of ribose to be obtained, we studied them by means of ^{13}C-NMR spectroscopy.

In ^{13}C-NMR spectra of aqueous solutions of D-lyxose, D-mannose, L-ribose, D-talose and D-allose signals can reliably be assigned to individual carbon atoms[2,3]. The same aldoses measured in aqueous solutions of ammonium molybdate also give signals shifted towards lower magnetic field (Table I). Similar shift in ^{13}C-NMR spectra is known in the case of complexes of saccharides with some lanthanoides[4] as well as in those of boric acid with saccharides having *cis*-arrangement of hydroxyl groups[5]. The shift of signals in ^{13}C-NMR spectra of aldoses represents thus another evidence for complexation of the measured aldoses with molybdate ions. Under the given experimental conditions it is possible to show that (according to the height of the signals in spectra) about 40% aldose is bound in molybdate complex (Fig. 1).

The shift of signals in ^{13}C-NMR spectrum is due to the respective hydroxyl at the considered carbon atom being bound in molybdate complex and to the aldose being forced into a certain conformation, the non-bonding interactions being important, too. Analysis of vicinal interaction constants obtained from ^{1}H-NMR spectra showed that both D-mannose and D-lyxose molecules in molybdate complexes are present

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TABLE I

Chemical Shifts (ppm, δ scale) in ^{13}C-NMR Spectra of Aldoses before (*a*) and after (*b*) Complexation with Ammonium Molybdate

Aldose		$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
β-D-Lyxose	*a*	94·98	70·84	73·50	69·38	64·96	—
	b	112·27	87·78	84·14	81·25	68·42	—
β-D-Mannose	*a*	94·49	72·03	73·91	67·40	76·96	61·83
	b	112·09	88·24	84·12	79.23	79·77	64·83
β-L-Ribose	*a*	94·62	69·69	68·08	71·82	63·79	—
	b	102·39	80·11	86·08	75·88	66·01	—
α-D-Talose	*a*	95·46	71·83	71·45	65·92	71·96	62·26
	b	103·33	84·74	86·54	80·09	77·39	63·59
β-D-Allose	*a*	94·26	72·07	72·07	67·68	74·43	62·07
	b	102·79	79·98	86·62	77·75	76·29	63·55

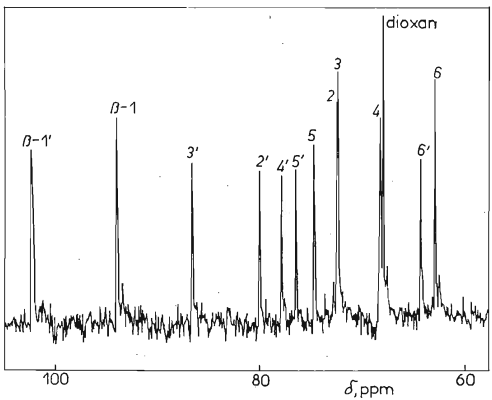

FIG. 1

^{13}C-NMR Spectrum of D-Allose Measured in Deuterium Oxide in the Presence of Ammonium Molybdate

The individual numbers and apostrophized numbers denote signals of ^{13}C atoms of the aldose and its molybdate complex, respectively.

exclusively in their β-pyranoid structures with conformation between the extreme conformers $B_{5,2}$ and $^{4,1}B$, *i.e.* conformation close to the $^{1}S_5$ conformer[1]. On the basis of these results the shift of the individual signals in ^{13}C-NMR spectrum of D-mannose and D-lyxose can be considered to be due to formation of molybdate complex with the hydroxyl groups at $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$ carbon atoms of the aldose and to formation of the aldose conformation close to the $^{1}S_5$ conformer. Specific rotation of aldoses of the homomorphous series of lyxose in aqueous solutions of ammonium molybdate (*a*) compared with that in water (*b*) shows the values shifted significantly to those of β-anomers of their pyranoid structures[6] ($[\alpha]_D$. L-lyxose *a*) +59°, *b*) +14°; L-mannose *a*) +35°, *b*) −14·5°; D-*glycero*-L-*manno*-heptose *a*) +0·5°, *b*) −14°). Therefrom it follows that the hemiacetal hydroxyl group and that at $C_{(2)}$ have *cis*-arrangement in the structure entering in the molybdate complex. This presumption agrees with results of the analysis of ^{1}H-NMR spectra of D-mannose and D-lyxose in molybdate complexes. Values of specific rotation of ribose, talose, L-*glycero*-L-*talo*-heptose and allose in ammonium molybdate solution are shifted in favour of the anomer having *trans*-arrangement of hydroxyl groups at $C_{(1)}$ and $C_{(2)}$ atoms ($[\alpha]_D$, D-ribose *a*) −77·5°, *b*) −18·7°; D-tallose *a*) +61·2°, *b*) +21·2°; L-*glycero*-L-*talo*-heptose *a*) −46·2°, *b*) −15°; D-allose *a*) −62°, *b*) +14·5°). Different behaviour of these two groups of aldoses in molybdate complexes is also observed in signal shifts of their ^{13}C-NMR spectra (Fig. 2).

Aldopentoses and aldohexoses with *cis-cis* arrangement of hydroxyl groups at carbon atoms 1−3 react with molybdate ions at pH 5 to give complexes which are

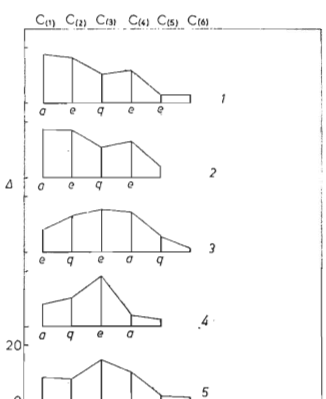

FIG. 2

Changes of Chemical Shifts in ^{13}C-NMR Spectra of Aldoses after Complexation with Ammonium Molybdate

Δ = C(complex) − C(free) [ppm]; *a* axial, *e* equatorial, *q* quasi. *1* β-D-manopyranose $^{1}S_5$ *2* β-D-lyxopyranose $^{1}S_5$ *3* α-D-talopyranose $^{1}S_3$ *4* β-D-ribopyranose $^{1}S_3$ *5* β-D-allopyranose $^{1}S_3$.

mobile during paper electrophoresis (ribose, lyxose, mannose, gulose, talose); the aldoses which do not fulfil this conditions are not mobile (arabinose, xylose, altrose, glucose, galactose)[7]. In formation of molybdate complexes lyxose and mannose fulfil the condition of *cis-cis* arrangement of hydroxyl groups at $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$ in the form of their β-anomers, which was proved by polarimetry and ^{1}H-NMR spectroscopy[1,6]. In the case of pyranoid structures of ribose, talose and allose two *cis-cis* arrangements are possible between the hydroxyl groups forming the molybdate complexes *viz.* at $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$ or $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$. In the former case hydroxyl group at $C_{(1)}$ would have to take part in formation of the molybdate complex. However, results of polarimetry and ^{13}C-NMR spectroscopy show that in molybdate complexes of ribose, talose and allose the latter case of *cis-cis* arrangement of the aldose hydroxyl groups only is significant, the $C_{(1)}$ hydroxyl group being in *trans* position with respect to the $C_{(2)}$ hydroxyl group.

The obtained results allow to state that ribose, talose and allose act as trident donors in their molybdate complexes using the hydroxyl groups at $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$ and assuming probably the conformation $^1S_3$ with $2q - 3e - 4a$ arrangement of the three hydroxyl groups.

EXPERIMENTAL

The ^{13}C-NMR spectra of the studied aldoses were measured with a Varian CFT-20 spectrometer with spectral width 5000 Hz, average accumulation number 10000, pulse width 7 μs (8192 data points) using the noise decoupling method. Dioxane was used as internal standard. Chemical shift of dioxane was 67·40 ppm with respect to TMS (tetramethylsilane). All the values of chemical shift are recalculated with respect to TMS and are given with the accuracy 0·06 ppm. Diameter of the cells used was 8 mm, temperature of the measurements 35—40°C. Samples of the aldoses were measured in D_2O, for complexation with molybdate ions 100 mg aldose and 100 mg ammonium molybdate were dissolved in 1·5 ml D_2O.

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