Reactions of Saccharides Catalyzed by Molybdate Ions XLVI.* Molybdate Complexes of Aldotetroses, 5-Deoxy-L-arabinose, and 5-Deoxy-L-ribose

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It was proved by means of ^1H, ^{13}C and ^{95}Mo NMR spectroscopy that in aqueous solution of ammonium molybdate D-threose, D-erythrose, 5-deoxy-L-arabinose, and 5-deoxy-L-ribose in acyclic hydrated form enter binuclear tetradentate molybdate complexes. Arrangement of D-threose and 5-deoxy-L-arabinose carbon chain at the site of complexation was found to be zigzag, whilst that of D-erythrose and 5-deoxy-L-ribose sickle. Molybdate complexes of respective aldoses are present in two conformations, formation of which is explained by different linkage modes of aldose to the binuclear molybdate core.

Molybdate complexes of alditols [1—3], aldoses [3—10], and 2-ketoses [3, 11] in aqueous solutions were examined by ^1H, ^{13}C and ^{95}Mo NMR spectroscopy. Alditols entered binuclear tetradentate molybdate complexes with sickle and zig-zag spatial arrangements of the carbon chain at the site of complexation; these arrangements can be recognized also by means of ^{95}Mo NMR spectroscopy [1—3]. Aldopentoses, -hexoses, and -heptoses of lyxose and ribose homomorphous series respectively, entered molybdate complexes preferentially in a pyranoid form with donor hydroxyl groups at C-1, C-2, C-3 and C-2, C-3, C-4, respectively. In smaller extent these aldoses in acyclic hydrated form gave rise to a binuclear tetradentate molybdate complex [4—9]. Aldopentoses, -hexoses, and -heptoses of arabinose homomorphous series as well as D-xylose and D-glucose in the acyclic hydrated form enter binuclear tetradentate molybdate complexes only [8, 9].

Molybdate complexes of aldotetroses, 5-deoxy-L-arabinose, and 5-deoxy-L-ribose were examined by ^{13}C NMR spectroscopy only, and therefore, structural features of these complexes were somehow misinterpreted [10]. This paper deals with the structure elucidation of the molybdate complexes of D-threose (*I*), 5-deoxy-L-arabinose (*II*), 5-deoxy-L-arabinitol (*III*), D-erythrose (*IV*), 5-deoxy-L-ribose (*V*), and 1-deoxy-L-ribitol (*VI*) by means of various NMR techniques using results concerning molybdate complexes of monosaccharides investigated so far.

Formation of binuclear tetradentate molybdate complexes with acyclic hydrated structure of aldopentose, -hexose, and -heptose was found in all homomorphous series. In this type of complex

hydrated carbonyl group and three adjacent vicinal hydroxyl groups were involved [9]. Spatial arrangement of the carbon chain at the site of complexation of such complex depended on configuration of C-2 and C-3 carbon atoms (*erythro* and *threo*, respectively), and could be close to sickle and zigzag, respectively, with characteristic values of the NMR data. In ^{13}C NMR spectra the chemical shift of C-1 carbon atom (sickle $\delta = 95.4$ and zig-zag $\delta = 99.7$) represented a diagnostic value. The chemical shift of the proton of hydrated carbonyl group bound to the complex varied within $\delta = 5.60$ and 5.37.

In aqueous solutions aldotetroses, 5-deoxy-L-arabinose, and 5-deoxy-L-ribose in the absence of molybdate ions appeared preferentially in furanoid structure, although a great amount of acyclic hydrated (hydrate) as well as not hydrated (aldehyde) forms was present. Content of the hydrate for the D-threose and D-erythrose was found to be 10—12 % [12, 13], that of 5-deoxy-L-arabinose and 5-deoxy-L-ribose 0.6 % and 0.8 %, respectively [14]. Therefore, formation of binuclear tetradentate molybdate complex of these acyclic hydrated forms could be anticipated.

The chemical shifts of C-1 atoms of the molybdate complexes of aldoses under investigation were in a very good accordance with the above-mentioned characteristic values for the particular arrangements of the carbon chain in these complexes (Table 1).

We succeeded in estimation of the complete NMR data of the binuclear tetradentate molybdate complex with sickle arrangement in the case of D-lyxose and D-mannose only due to a relatively high content of such complex in solution [9]. The ^1H and ^{13}C NMR data of molybdate complexes of D-erythrose and 5-deoxy-L-ribose are in good ac-

cordance with them (Tables 1 and 2) and the coupling constants values in ^{1}H NMR spectra are in line with the presumed *gauche-gauche-gauche* orientation of the hydroxyl groups in the sickle spatial arrangement of the carbon chain [15, 16].

In ^{1}H NMR spectra of D-xylose, D-glucose, and D-glucitol broad band signals were characteristic of binuclear tetradentate molybdate complexes with zig-zag arrangement from which coupling constants could not be extracted [1, 9]. However, the values of all coupling constants for this type of complex were obtained by means of 1D COSY and 1D relayed COSY experiments for 5-deoxy-L-arabinose (Table 2). Their values agreed with those reported for *gauche-gauche-gauche* orientation of hydroxyl groups with the planar zig-zag arrangement of the carbon chain [15, 16].

The one-bond coupling constants values $^1J_{C-1, H-1}$ for cyclic furanoid and acyclic hydrated forms varied between 172—174 and 162—164 Hz,

respectively [17]. Values of the one-bond coupling constants for the particular aldoses under study give evidence unambiguously of the acyclic structures of these complexes (Table 1).

This expected binuclear tetradentate molybdate complex in the case of D-erythrose and 5-deoxy-L-ribose as well as D-threose and 5-deoxy-L-arabinose was denoted as E_1 and F_1 conformer, respectively. It came from the fact that the NMR spectra contain also signals of another complex represented by a small amount. We denoted it as conformer E_2 and F_2, respectively. For 5-deoxy-L-ribose the values of the coupling constants of conformer E_1 are identical with those of E_2. In the case of 5-deoxy-L-arabinose coupling constants values of F_1 are very close to those of F_2 conformer (Table 2). ^{13}C NMR chemical shifts as well as one-bond coupling constants $^1J_{C-1, H-1}$ of both conformers are also characteristic of the complex having an acyclic structure (Table 1).

Table 1. ^{13}C NMR Data of Aldoses and Their Corresponding Alditols in Molybdate Complexes

Saccharide	Conformer[a]	Chemical shift δ					Coupling constants $^1J_{C-1, H-1}$/Hz	Ratio of conformers
		C-1	C-2	C-3	C-4	C-5		
D-Threose (*I*)	F_1	99.7	86.0	81.1	76.2	–	167.3	7 : 3
	F_2	98.2	83.4	76.8	76.2	–	167.3	
Threitol[b] (*VIII*)	–	77.0	83.4	83.4	77.0	–	–	–
5-Deoxy-L-arabinose (*II*)	F_1	99.9	84.1	81.0*	80.9*	16.6	168.4	7 : 3
	F_2	98.3	78.5	80.0	80.9	16.9	**	
5-Deoxy-L-arabinitol (*III*)	–	76.4	77.5	85.7	81.0	16.8	–	
D-Erythrose (*IV*)	E_1	95.3	94.1	81.6	72.5	–	165.3	8 : 2
	E_2	98.9	90.0*	88.0*	69.9	–	166.1	
Erythritol[c] (*IX*)	–	70.2	91.7	82.7	73.2	–	–	–
5-Deoxy-L-ribose (*V*)	E_1	95.4	92.6	84.6	81.4	17.9	166.3	9 : 1
	E_2	95.4	86.3	94.1	78.5	19.2	**	
1-Deoxy-L-ribitol (*VI*)	–	70.6	90.9	84.8	82.0	18.0	–	
D-Ribose (*VII*)	E_1	95.7	92.6	84.5	82.0	62.8	**	

a) Sickle and zig-zag arrangements of the carbon chains at the complexation site are denoted E and F, respectively; b) Ref. [2]; c) Ref. [1]; *interchangeable signals; **not assigned.

Table 2. ^{1}H NMR Data of Aldoses and Their Corresponding Alditols in Molybdate Complexes

Saccharide	Conformer	Chemical shift δ							Coupling constants J/Hz					
		H-1'	H-1	H-2	H-3	H-4	H-4'	H-5	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{3,4'}$	$J_{4,4'}$	$J_{4,5}$
I	F_1	–	5.46	4.24	4.24	a	a	–	0.2	**	**	**	**	–
	F_2	–	5.58	4.12	4.08	4.25	4.10	–	2.2	0.2				–
II	F_1	–	5.40	4.01	4.42	4.43	–	1.23	0.5	1.9	1.9	–	–	6.4
	F_2	–	5.60	4.33	4.49	4.43	–	1.59	2.2	1.2	2.0	–	–	6.2
III	–	4.18	4.18	4.60	4.20	4.46	–	1.38	*	*	2.0	–	–	6.5
IV	E_1		5.40	4.65	4.83	4.49	4.45	–	0.9	4.4	4.6	1.3	– 10.6	–
	E_2		5.79	4.74*	4.85*	**	**	–	0.2	**	**	**	**	–
IX	–	4.52	4.52	4.83	4.74	4.29	4.05	–	**	4.5	0.2	2.7	– 10.2	
V	E_1		5.53	4.74	4.63	4.74	–	1.23	0.6	4.0	4.6	–	–	6.5
	E_2		5.42	4.56	4.64	4.70	–	1.34	0.6	4.0	4.6	–	–	**
VI	–	4.46	4.02	4.85	4.62	4.84	–	1.29	0.2	4.4	4.3	–	–	6.9

a) Signals overlapped in δ = 4.10—4.25 range; *interchangeable signals; **not resolved.

Formation of two conformers was observed in the case of binuclear tetradentate complexes with sickle arrangement in arabinose homomorphous series with donor hydroxyl groups at C-2, C-3, C-4, and C-5 [8] as well as in the case of alditols with donor hydroxyls of *arabino* arrangement [2]. The former formation of two conformers was explained by different spatial orientation of parts of the molecule of aldose which are not involved in the complex [8]. *Verchere et al.* [2] explained it by the change of spatial orientation of one of both lateral carbon atoms differing in the substituent size; preferred is the conformer the twisted carbon atom of which bears a smaller substituent.

Appearance of deformed octahedra is a characteristic feature of molybdenum [17]; the asymmetry of a binuclear molybdate core was evidenced also by its different bond lengths and bond angles determined by X-ray structural analysis of the molybdate complex of mannitol [18 , 19] and erythritol [20].

In ^{1}H NMR spectra the coupling constants of both conformers of 5-deoxy-L-arabinose as well as 5-deoxy-L-ribose are in very good accordance (Table 2), nevertheless remarkable changes in the chemical shift values for the particular hydrogen and carbon atoms occur. These changes reflect different shielding of nuclei which may be caused by different binding mode of aldose to asymmetric binuclear molybdate core. In the structure of molybdate complex of erythritol proved by X-ray analysis (Fig. 1) [20] with regard to the symmetry of the erythritol molecule the numbering of the carbon atoms may be reversed without any change. However, in the case of acyclic hydrated forms of aldoses such a different mode of binding of aldose to asymmetric binuclear core is manifested by formation of two conformers E_1, E_2 and F_1, F_2, respectively. Mutual ratio of conformers F_1 and F_2 of D-threose and 5-deoxy-L-arabinose molybdate complexes with zig-zag arrangement was 7 : 3; in complexes with sickle arrangement of D-erythrose and 5-deoxy-L-ribose E_1 conformer is more preferred (Table 1). Mutual ratio of conformers is not temperature-dependent (2, 25, and 40 °C). It is noteworthy that formation of two conformers of 5-deoxy-L-arabinitol and 1-deoxy-L-ribitol was not evidenced in their molybdate complexes.

Identification of ^{13}C NMR signals of the binuclear tetradentate complex of the acyclic hydrated form of D-ribose (< 10 %) in aqueous ammonium molybdate was made possible from the ^{13}C NMR data of the E_1 conformer of 5-deoxy-L-ribose and 1-deoxy-L-ribitol in molybdate complexes (Table 1). Existence of this complex was presumed in our preceding paper [9] from the presence of a singlet signal at δ = 5.50 in the ^{1}H NMR spectrum.
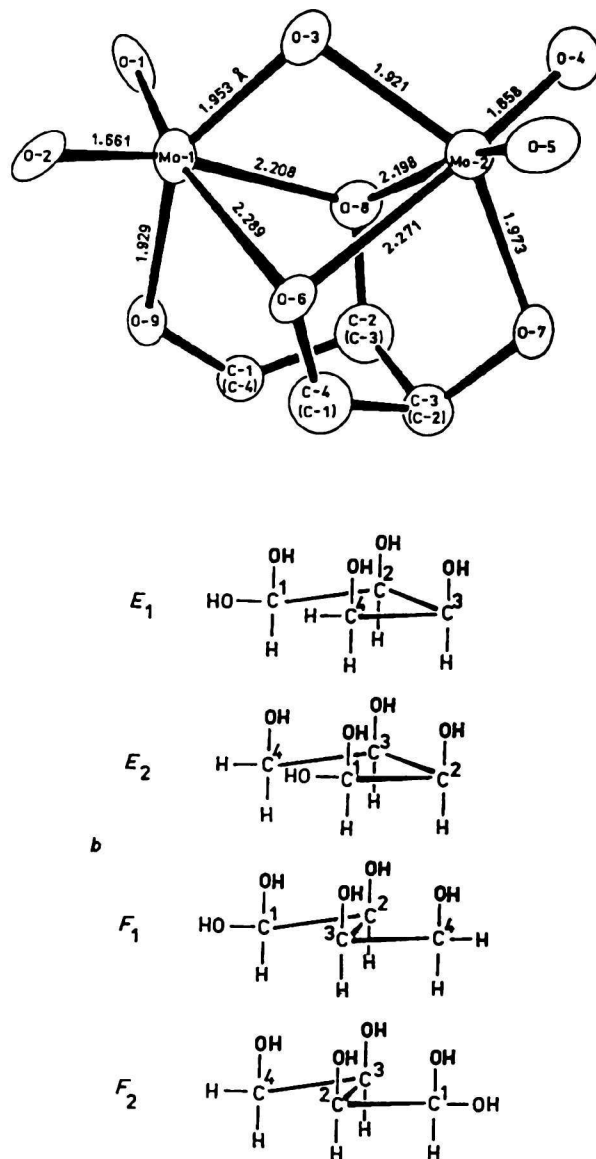

Fig. 1. a) Binuclear tetradentate molybdate complex of the symmetric erythritol molecule proposed on the basis of X-ray analysis [20]. Due to the symmetry of the erythritol molecule numbering of carbon atoms may be reversed. b) Two pairs of conformers (E_1, E_2 and F_1, F_2) were formed as a consequence of asymmetry of the hydrated forms of erythrose and threose molecules, respectively.

Table 3. ^{95}Mo NMR Data of Aldoses and Their Corresponding Alditols in Molybdate Complexes

Saccharide	Chemical shift δ	Signal half-width $W_{1/2}$/Hz
I	21	290
II	24	370
III [3]	19	280
IV	31	390
V	29	290
VI	31	170

The chemical shift values in the ^{95}Mo NMR spectra of molybdate complexes of aldoses and their corresponding alditols under study were in good accordance with the characteristic values for binuclear tetradentate complexes with sickle ($\delta = 25-34$ [3], $\delta = 30-34$ [2]) or zig-zag ($\delta = 18-20$ [3], $\delta = 22$ [2]) arrangements at the complexation site (Table 3).

EXPERIMENTAL

Deuterium oxide solutions containing the saccharide and ammonium molybdate (($NH_4)_6Mo_7O_{24}$ $\cdot 4H_2O$) in a 1 mol saccharide to 2 mol molybdenum ratio were measured with a Bruker AM-300 FT NMR spectrometer at 298 K. Methanol ($\delta = 50.15$) and TSP (sodium 3-(trimethylsilyl)propionate, $\delta = 0.00$) were internal references for ^{13}C (75 MHz) and ^{1}H NMR (300 MHz) spectra, digital resolution 1.9 Hz and 0.12 Hz per point, respectively. Spectral parameters for the ^{95}Mo NMR spectra (19.56 MHz) were identical with those reported in Ref. [3].

Following techniques of the standard program of the Bruker equipment were employed for assignment of signals: ^{13}C NMR spectra: CH COSY with decoupling in the F1 domain, DEPT, gated decoupling ^{13}C NMR spectrum with the preserved NOE and semiselective INEPT; ^{1}H NMR spectra: 1D homocorrelated spectroscopy (1D-COSY and 1D-relayed COSY) [21] and 2D homocorrelated spectroscopy. Fixed delays in 1D-COSY and 1D-relayed COSY experiments for the selective magnetization transfer were calculated from the known values of coupling constants.

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