

Reactions of saccharides catalyzed by molybdate ions XLIII.* ^{95}Mo NMR spectra of the molybdate complexes of alditols and aldoses

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Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday

The tetradentate molybdate complexes of alditols with the sickle arrangement of the carbon chain in the site of complexation, formed in the aqueous solutions of ammonium molybdate have in the ^{95}Mo NMR spectra the signals with chemical shifts in the interval of 25—34 ppm, while those with the zig-zag arrangement in the interval of 18—20 ppm. Aldoses of the homomorphous series of lyxose, ribose, and arabinose in the molybdate complexes display ^{95}Mo NMR spectra which are characteristic of each homomorphous series.

В ^{95}Mo ЯМР спектрах водных растворов молибдата аммония сигналы двухъядерных тетраденатных молибдатных комплексов алдитолов с серпообразной формой углеродной цепи в месте комплексации находятся на расстоянии 25—34 ппм и зигзагообразной формой, — на расстоянии 18—20 ппм. Альдозы гомоморфных рядов ликсозы, рибозы и арабинозы образуют в молибдатных комплексах характерные ^{95}Mo ЯМР спектры для каждого гомоморфного ряда.

Recently we have carried out studies of the aqueous solutions of the molybdate complexes of alditols [1], aldoses of the homomorphous series of ribose and arabinose [2], aldoses of xylose and lyxose homomorphous series [3] and of 2-ketoses [4] by means of ^1H and ^{13}C NMR spectroscopy. Alditols form two types of the molybdate complexes from the aspect of the spatial arrangement of the carbon chain [1]. Pentoses, hexoses, and heptoses produce characteristic molybdate complexes within the individual homomorphous series [2—4].

In the last ten years ^{95}Mo NMR spectroscopy has been used for the investigation of the molybdenum complexes with various organic substances [5]. *Verchere* and *Chapelle* [6] applied ^{95}Mo NMR spectroscopy to a study of the molybdate complexes of D-lyxose, D-mannose, and L-rhamnose and came to the conclusion that those were binuclear molybdate complexes.

* For Part *XLII* see Ref. [3].

In our work we investigated by means of ^{95}Mo NMR spectroscopy the molybdate complexes of the following saccharides: erythritol (*I*), L-arabinitol (*II*), 5-deoxy-D-arabinitol (*III*), ribitol (*IV*), xylitol (*V*), D-glucitol (*VI*), 2-deoxy-D-arabino-hexitol (*VII*), 6-deoxy-L-glucitol (*VIII*), D-mannitol (*IX*), 1-deoxy-L-mannitol (*X*), galactitol (*XI*), D-altritol (*XII*), perseitol (*XIII*), volemitol (*XIV*), D-lyxose (*XV*), D-mannose (*XVI*), D-glycero-D-gulo-heptose (*XVII*), D-tagatose (*XVIII*), D-manno-2-heptulose (*XIX*), D-ribose (*XX*), D-talose (*XXI*), D-arabinose (*XXII*), and D-galactose (*XXIII*).

It was proved by means of X-ray structural analysis of the molybdate complexes that D-mannitol formed binuclear molybdate complex with three vicinal secondary hydroxyl groups and the adjacent primary hydroxyl group [7, 8]. Two molybdate octahedra are coordinated with six oxygen atoms, three of them being common for both octahedra (the octahedra share the common face). Oxygen atoms of the hydroxyl groups bound to the carbon atoms C-1 and C-3 of D-mannitol molecule are located on the common edge of both octahedra (Fig. 1*a*), while the oxygen atoms of the hydroxyl groups linked to the carbon atoms C-2 and C-4 represent the corners of the octahedra [7, 8]. The shape of the carbon chain of the formed molybdate complex has a sickle arrangement and is schematically presented in Fig. 1*a*. Using ^1H and ^{13}C NMR spectroscopy it was found that alditols in aqueous solutions form molybdate complexes with four vicinal hydroxyl groups, the shape of the carbon chain having sickle or zig-zag spatial arrangement (Fig. 1*a* or 1*b*) [1]. In the case of the alditols producing complexes with both zig-zag and sickle arrangements of the carbon chain, the latter type of the complexes is preferred at 25°C, while at the increased temperature (70–80°C) the ratio of the molybdate complexes with sickle and zig-zag shapes becomes equal [1].

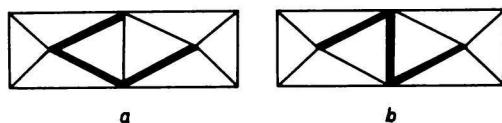


Fig. 1. Schematic illustration of two molybdate octahedra, the above view. The octahedra are below the sheet plane joined with the common face. The shape of the carbon chain of the alditol in the site of complexation of its hydroxyl groups is graphically emphasized.

a) Sickie and b) zig-zag arrangement.

In the ^{95}Mo NMR data of the molybdate complexes of alditols (Table 1) a dependence on the spatial arrangement of the carbon chain of the produced alditol molybdate complex is evident as well. In the most cases alditols (*II*, *IV*, *VII*, *IX*–*XIV*) with the sickie arrangement of the carbon chain in the molybdate

Table 1

⁹⁵Mo NMR data of the molybdate complexes of alditols*

Alditol	Chemical shift/ppm (Relative intensity of the signal)		Signal half-width ^a $W_{1/2}$ /Hz	Donor hydroxyl groups	Shape of the carbon chain in the complex
<i>I</i>	31		130	1, 2, 3, 4	sickle
<i>II</i>	31 (1)	27 (0.8)	230	2, 3, 4, 5	sickle
<i>III</i>		19	280	1, 2, 3, 4	zig-zag
<i>IV</i>	34 (1)	27 (1)	260	2, 3, 4, 5	sickle
<i>V</i>		20	160	1, 2, 3, 4	zig-zag
<i>VI</i>	33 (1)	29 (1)	520	3, 4, 5, 6; 1, 2, 3, 4	sickle; zig-zag
<i>VII</i>	33 (1)	25 (0.7)	360	3, 4, 5, 6	sickle
<i>VIII</i>		18	450	1, 2, 3, 4	zig-zag
<i>IX</i>	33 (1)	29 (1)	320	3, 4, 5, 6	sickle
<i>X</i>	34 (0.7)	26 (1)	340	3, 4, 5, 6	sickle
<i>XI</i>	32 (1)	26 (0.9)	260	2, 3, 4, 5	sickle
<i>XII</i>	33 (1)	28 (0.7)	230	2, 3, 4, 5	sickle
<i>XIII</i>	32 (0.8)	27 (1)	300	2, 3, 4, 5; 3, 4, 5, 6	sickle; sickle
<i>XIV</i>	33 (1)	29 (1)	240	4, 5, 6, 7; 3, 4, 5, 6	sickle; sickle

* ¹H and ¹³C NMR data of these complexes have been determined in Ref. [1].^a) In relation to the less intensive signal.

complex have in the ^{95}Mo NMR spectra two signals with the chemical shifts 31—34 and 25—29 ppm. In the case of the molybdate complex of erythritol (*I*) only one signal ($\delta = 31$ ppm) with a relatively small half-width (130 Hz) is present, which implies that the produced binuclear molybdate complex is significantly symmetrical. Alditols *III*, *V*, and *VIII* that have zig-zag shape of the carbon chain in the molybdate complexes exhibit in ^{95}Mo NMR spectra only one signal with the chemical shift of 18—20 ppm. D-Glucitol (*VI*) that produces two types of complexes (sickle and zig-zag) [1] contains in its ^{95}Mo NMR spectra signals characteristic of the sickle arrangement ($\delta = 29$ and 33 ppm) as well as the signal characterizing zig-zag arrangement ($\delta = 19$ ppm).

During the investigation of the temperature dependence of the chemical shifts and half-width values of the signals of *II* and *VI* it was discovered that increasing temperature from 25 °C to 60 °C leads to the shift of the signals downfield ($\delta \approx 5$ —10 ppm) and to narrowing of the half-width of the signals (by *ca.* 70—80 Hz). In the case of D-glucitol (*VI*) simultaneously with the increasing of the temperature, equalization of the ratio of the signals characteristic of the molybdate complexes of glucitol with the sickle and zig-zag arrangements takes place, which is confirmed by the ^{13}C NMR data [1].

Characterization of the molybdate complexes of aldoses and 2-ketoses by their ^{95}Mo NMR spectra is extremely difficult since they produce more types of molybdate complexes [2—4]. It follows from the results of ^1H and ^{13}C NMR measurements that the preferable type of the molybdate complexes of the aldoses of lyxose homomorphous series is the one involving hemiacetal hydroxyl group and the hydroxyl groups linked to the carbon atoms C-2 and C-3 of the pyranoid form of the aldose [3]. In the case of D-tagatose (*XVIII*) and D-manno-2-heptulose (*XIX*) there occurs preferable formation of a complex involving hemiacetal hydroxyl group and the hydroxyl groups linked to the carbon atoms C-3 and C-4 of their pyranoid forms [4]. For aldoses *XV*—*XVII* as well as 2-ketoses *XVIII* and *XIX* the molybdate complexes of which involve hemiacetal hydroxyl group and two adjacent vicinal hydroxyl groups of the pyranoid cycle of the aldose or 2-ketose, two characteristic signals with the chemical shifts 29—35 and 41—44 ppm are observed in the ^{95}Mo NMR spectra (Table 2). D-Ribose (*XX*) and D-talose (*XXI*) have donor hydroxyl groups involved in the molybdate complex that are linked to the carbon atoms C-2, C-3, and C-4 of the pyranoid structure [2]. The values of ^{95}Mo chemical shifts of the complexes *XX* and *XXI* essentially differ from those of the complexes *XV*—*XIX*, which have hemiacetal hydroxyl group involved in them (Table 2).

The aldoses of arabinose homomorphous series join the molybdate complexes in acyclic structures and produce tetradentate molybdate complexes employing preferably the hydroxyl groups linked to the carbons C-2, C-3, C-4, and C-5 [2]. The shape of the carbon chain in the formed molybdate complexes has a sickle spatial arrangement. The chemical shift values of the complexes of

Table 2

⁹⁵Mo NMR data of the molybdate complexes of aldoses and 2-ketoses

Saccharide	Chemical shift δ /ppm		Signal half-width $W_{1/2}$ /Hz	Ratio of relative intensities of the signals
<i>XV</i>	41	33	320	1:1
<i>XVI</i>	41	29	140 200	1:2
<i>XVII</i>	41	32	280*	1:0.8
<i>XVIII</i>	44	35	130 130	1:1
<i>XIX</i>	44	29	120 120	1:1
<i>XX</i>	28	9	220 180	2:1
<i>XXI</i>	24	0	380 460	1:2
<i>XXII</i>	30		300	
<i>XXIII</i>	30		320	

* In relation to the less intensive signal.

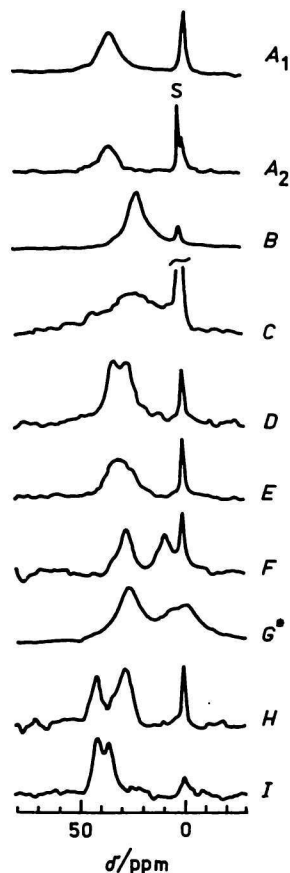


Fig. 2. ⁹⁵Mo NMR spectra of: *A*₁ — ammonium molybdate; *A*₂ — ammonium molybdate with sodium molybdate as external standard (S); standard and of the molybdate complexes of *B*. xylitol (*V*), *C*. D-xylose, *D*. galactitol (*XI*), *E*. D-galactose (*XXIII*), *F*. D-ribose (*XX*), *G**. D-talose (*XXI*; without the standard), *H*. D-mannose (*XVI*), *I*. D-glycero-D-gulo-heptose (*XVII*).

D-arabinose (XXII) and D-galactose (XXIII) in the ^{95}Mo NMR spectra (Table 2) are in good accordance with the chemical shift values of the molybdate complexes of the alditols with a sickle arrangement of the carbon chain in the molybdate complex (Table 1, Fig. 2).

The aldoses of xylose homomorphous series join the molybdate complexes also in acyclic structures as the tetradentate donors with the hydrated carbonyl group and vicinal hydroxyl groups linked to the carbon atoms C-2, C-3, and C-4. The shape of the carbon chain in the molybdate complexes of D-xylose and D-glucose has a zig-zag spatial arrangement [3]. The content of the produced molybdate complex of these aldoses is usually small ($< 15\%$). That is a reason why noncomplexed ammonium molybdate partially interferes at the conditions of measurement of ^{95}Mo NMR spectra as well. In the case of D-xylose molybdate complex, a position of the signal in ^{95}Mo NMR spectrum implies that this complex has a zig-zag arrangement of the carbon chain in the site of complexation, similarly as it is with xylitol (Fig. 2).

The ^{95}Mo NMR signals of the molybdate complexes of the alditols with a sickle arrangement of the carbon chain have different positions from those of the molybdate complexes with a zig-zag arrangement. ^{95}Mo NMR spectra of the aldoses of homomorphous series of lyxose and ribose that form molybdate complexes prevailing in pyranoid structures, differ significantly one from another as well. The aldoses of arabinose homomorphous series occur in tetradentate molybdate complexes in the acyclic structures and their ^{95}Mo NMR spectra are analogous to those of the molybdate complexes of the alditols with a sickle arrangement of the carbon chain in the site of complexation. Similar relation can be observed between the molybdate complexes of aldoses of xylose homomorphous series and those of the alditols with a zig-zag arrangement of the carbon chain in the site of complexation.

Experimental

^{95}Mo NMR spectra of the molybdate complexes of aldoses, 2-ketoses, and alditols in aqueous solutions of ammonium molybdate (mass ratio = 10 : 1) were measured using FT-NMR spectrometer AM-300 Bruker (19.56 MHz) at 298 K or 333 K with the following parameters: spectral width 25 000 Hz, 2K data point completed with zero filling to 4K, digital resolution 12.2 Hz per point, pulse width corresponding to 45° flip angle, acquisition time 0.04 s. As an external standard aqueous solution of 2 M- Na_2MoO_4 ($\delta = 0$ ppm) was used. In order to limit acoustic probe ringing, 150 μs pre-acquisition delay was used.

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