

# Reactions of saccharides catalyzed by molybdate ions XLI.\* NMR spectra of 2-ketoses in molybdate complexes

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*Dedicated to Professor P. Kristian, DrSc., in honour of his 60th birthday*

It was proved by means of NMR spectroscopy that *D-threo*-2-pentulose, *D*-psicose, *D*-fructose, *L*-sorbose, *D*-tagatose, *D-manno*-2-heptulose, and *D-gluco*-2-heptulose form with ammonium molybdate in aqueous solutions molybdate complexes in cyclic structures involving hydroxyl groups bound to the carbon atoms C-1, C-2, and C-3. Together with this type of the complex involving the pyranoid structure, *D*-tagatose and *D-manno*-2-heptulose produce complexes involving hydroxyl groups attached to the carbons C-2, C-3, and C-4, while *D*-psicose forms a complex involving hydroxyl groups at C-3, C-4, and C-5. In the case of *L*-sorbose and *D*-fructose along with the tridentate molybdate complex with pyranoid structure, formation of acyclic tetradentate molybdate complex was observed involving the hydroxyl groups bound to the carbon atoms C-3, C-4, C-5, and C-6.

С помощью ЯМР спектроскопии показано, что *D-трео*-2-пентулоза, *D*-псигоза, *D*-фруктоза, *L*-сорбоза, *D*-тагатоза, *D-манно*-2-гептулоза и *D-глюко*-2-гептулоза образуют с молибденатом аммония в водных растворах молибдатные комплексы с циклической структурой с участием гидроксильных групп на атомах углерода C-1, C-2 и C-3. Наряду с комплексом такого типа, включающего пираноидную форму, *D*-тагатоза и *D-манно*-2-гептулоза образуют комплексы с участием гидроксильных групп, находящихся на углеродах C-2, C-3 и C-4, в то время, как *D*-псигоза образует комплекс, включающий гидроксильные группы на C-3, C-4 и C-5. В случае *L*-сорбозы и *D*-фруктозы наряду с тридентатным молибдатным комплексом с пираноидной структурой наблюдалось образование ациклического тетрадентатного молибдатного комплекса с участием гидроксильных групп, связанных с углеродными атомами C-3, C-4, C-5 и C-6.

Formation of the molybdate complexes of 2-ketoses can be observed due to the change of the specific rotation value which is maximal at pH 5.9 in comparison with the corresponding value in aqueous solutions [1]. As the result of

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the formation of molybdate complexes 2-ketohexoses (D-fructose, L-sorbose, D-tagatose) as well as 2-ketoheptoses (D-*gluco*-2-heptulose and D-*manno*-2-heptulose) become electrophoretically mobile (at pH 5.0) [2]. By means of circular dichroism technique complexation of D-fructose and L-sorbose with Mo(V) [3] was proved. Aqueous solutions of 2-ketohexoses [4–6] and 2-ketoheptoses [7] were investigated by means of NMR spectroscopy. However, the molybdate complexes of 2-ketoses have not been investigated by means of NMR spectroscopy as yet.

In this paper we report on the study of aqueous solutions of the molybdate complexes of D-psicose (*I*), D-tagatose (*II*), D-*manno*-2-heptulose (*III*), D-fructose (*IV*), L-sorbose (*V*), D-*gluco*-2-heptulose (*VI*), and D-*threo*-2-pentulose (*VII*) by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as well as on the basis of known NMR data of the molybdate complexes of the aldoses of homomorphous series of lyxose [8, 9], ribose, arabinose [10], and alditols [11].

$^1\text{H}$  and  $^{13}\text{C}$  NMR data obtained for D-psicose (*I*) in molybdate complex imply that the tridentate molybdate complex (*Ia*) is preferably formed in which hydroxyl groups bound to the carbon atoms C-1, C-2, and C-3 are involved (Tables 1 and 2, Scheme 1). Complex of this type with cyclic structure was found for all studied 2-ketoses (*Ia*—*VIa*). The content of this complex varies greatly for the different 2-ketoses in the range from 5 to 95 % (Table 1). It is generally recognized that in order to enable formation of such a complex 2-ketoses in pyranoid structures must contain hemiacetal hydroxyl group in axial position and hydroxyl group at C-3 carbon in equatorial position, or in positions very close to those (Scheme 1). D-*threo*-2-Pentulose (*VII*) in furanoid form also produces molybdate complex (*VIIb*) involving hydroxyl groups attached to carbon atoms C-1, C-2, and C-3 (Table 1).

D-Psicose along with preferable complex *Ia* forms in minor amount a complex of another type (*Ic*) which involves hydroxyl groups bound to carbon atoms C-3, C-4, and C-5 (Tables 1 and 2, Scheme 1). The molybdate complex *Ic* is similar to the molybdate complexes of the aldopentoses, aldohexoses, and aldohexoses of ribose homomorphous series. These aldoses form also tridentate molybdate complexes in pyranoid structures involving in complexation analogous hydroxyl groups bound in this case to carbon atoms C-2, C-3, and C-4, whereas the hemiacetal hydroxyl group and hydroxyl group at C-2 are *trans* [10].

In the case of D-tagatose (*II*) and D-*manno*-2-heptulose (*III*) along with molybdate complexes *IIa* and *IIIa*, preferable type of complexes *IIc* and *IIIc* is formed involving hydroxyl groups bound to carbon atoms C-2, C-3, and C-4 (Tables 1 and 2).  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of D-tagatose and D-*manno*-2-heptulose molybdate complexes are in good agreement with the data obtained for D-lyxose in molybdate complex ( $^{13}\text{C}$  NMR data,  $\delta/\text{ppm}$ : C-1 112.3, C-2 84.1, C-3 87.8,

Table 1

<sup>13</sup>C NMR data of the molybdate complexes of 2-ketoses

2-Ketose	Chemical shift $\delta$ /ppm							Complex form	Hydroxyl groups involved in the complex	2-Ketose portion in the complex/%
	C-1	C-2	C-3	C-4	C-5	C-6	C-7			
<i>I</i>	74.1	110.8	88.0	82.8	87.9	63.0		<i>Ia</i>	1,2,3	85
	65.7	105.2	81.3	87.0	76.0	66.4		<i>Ic</i>	3,4,5	10
<i>II</i>	73.5	110.7	88.6	81.5	83.7	62.7		<i>IIa</i>	1,2,3	20
	68.3	120.1	85.3	87.5	82.7	65.3		<i>IIc</i>	2,3,4	60
<i>III</i>	73.4	110.7	88.4	81.4	82.5	65.2	64.4	<i>IIIa</i>	1,2,3	40
	65.2	120.0	85.1	88.4	81.2	79.4	65.2	<i>IIIc</i>	2,3,4	50
<i>IV</i>	73.1	108.9	85.1	82.4	71.6	64.5		<i>IVa</i>	1,2,3	10
	67.9	215.3	84.8	82.7	91.8	70.7		<i>IVc</i>	3,4,5,6	10
<i>V</i>	68.3	109.0	88.7	82.7	84.6	63.8		<i>Va</i>	1,2,3	5
	63.9	215.1	85.2	82.7	83.5	76.1		<i>Vc</i>	3,4,5,6	15
<i>VI</i>	68.5	106.8	88.9	83.0	85.3	*	*	<i>VIa</i>	1,2,3	5
<i>VII</i>	71.6	108.8	85.2	82.9	64.3			<i>VIIb</i>	1,2,3	95

\* Unassigned signals.

Table 2

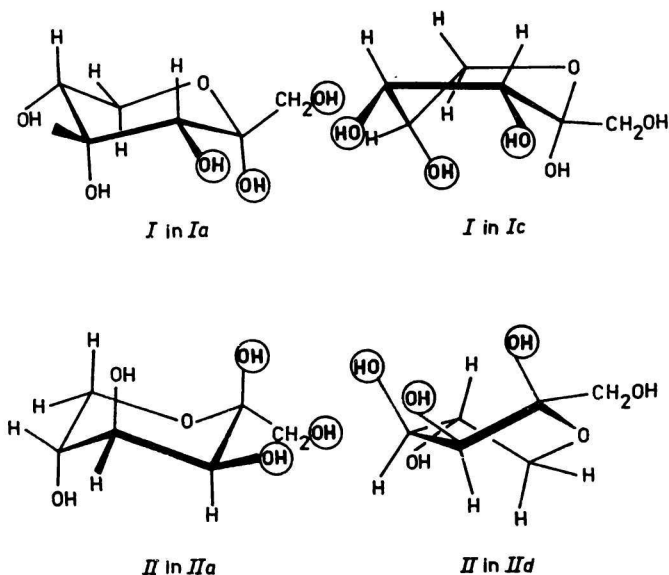
<sup>1</sup>H NMR data of the molybdate complexes of 2-ketoses

Complex form of 2-ketose	Chemical shift $\delta$ /ppm									
	H-1	H-1'	H-2	H-3	H-4	H-5	H-6	H-6'	H-7	H-7'
<i>Ia</i>	4.18*	4.18*	—	4.91	4.62	4.15*	3.60*	3.60*		
<i>Ic</i>	**	**	—	4.68	4.87	4.58	**	**		
<i>IIa</i>	**	**	—	4.84	4.69	**	**	**		
<i>IIId</i>	**	**	—	4.91	5.35	4.47	4.29	4.05		
<i>IIIa</i>	**	**	—	4.85	4.70	4.70	**		**	**
<i>IIIId</i>	**	**	—	4.90	5.36	4.37	**		**	**

Complex form of 2-ketose	Coupling constants $J$ /Hz									
	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{6,7}$	$J_{6,7'}$	$J_{7,7'}$	$^4J_{3,5}$	
<i>Ia</i>	3.9	0.2	**	**	**					
<i>Ic</i>	4.4	2.3	0.2	5.9	**				2.0	
<i>IIa</i>	3.7	0.2	**	**	**					
<i>IIId</i>	6.6	7.8	0.2	2.9	12.9					
<i>IIIa</i>	3.6	0.2	**	**	**					
<i>IIIId</i>	6.8	7.7	0.2			**	**	**		

\* Overlapped signals. \*\* Unassigned or unresolved signals.



Scheme 1

Forms of D-psicose (*I*) and D-tagatose (*II*) in molybdate complexes. Hydroxyl groups involved in complexation are graphically emphasized.

C-4 81.3, C-5 68.4;  $^1\text{H}$  NMR data,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ : H-1 6.18,  $J_{1,2}$  4.4, H-2 4.97,  $J_{2,3}$  6.8, H-3 5.36,  $J_{3,4}$  7.8, H-4 4.41,  $J_{4,5} < 0.2$ ,  $J_{4,5'}$  2.8, H-5 4.27, H-5' 4.04,  $J_{5,5'}$  12.8), in which D-lyxose has pyranoid structure with hydroxyl groups bound to carbon atoms C-1, C-2, and C-3 in the conformation close to  $^1S_5$ .

Hemiacetal hydroxyl group and hydroxyl group at C-2 in the molybdate complexes of the aldoses of lyxose homomorphous series are in *cis* position [8, 9]. This fact implies that D-tagatose and D-manno-2-heptulose in molybdate complexes *IIb* and *IIIb* also occur in pyranoid form with the conformation close to  $^2S_6$  (Scheme 1).

D-Fructose (*IV*) along with the molybdate complex of its cyclic form *IVa* produces large amount of the complex of acyclic structure involving hydroxyl groups bound to carbon atoms C-3, C-4, C-5, and C-6 (*IVe*), that is proved in  $^{13}\text{C}$  NMR spectrum by the presence of the signal belonging to the carbonyl group carbon  $\delta = 215.3$ . It follows from  $^{13}\text{C}$  NMR data that this binuclear tetradentate molybdate complex is similar to that of arabinose which involves hydroxyl groups attached to carbon atoms C-2, C-3, C-4, and C-5 [10]. NMR spectra of D-fructose contain along with the signals of the complexes *IVa* and *IVe*, also those indicating the presence of another type of the molybdate com-

plex of D-fructose with acyclic structure (*ca.* 10 %) which could not be unambiguously identified from the spectral data. Aldoses of arabinose homomorphous series produce binuclear tetradentate molybdate complexes in two conformations of acyclic forms involving hydroxyl groups bound to carbon atoms C-2, C-3, C-4, and C-5 [10]. It can be suggested that an unidentified molybdate complex of D-fructose may probably be the second conformer of acyclic form in which carbonyl group carbon has chemical shift 218.3 ppm.

In the case of L-sorbose (*V*) and D-*gluco*-2-heptulose (*VI*) along with molybdate complexes of the cyclic forms *Va* and *VIa*, complexes are formed in which *V* and *VI* occur in acyclic forms. The molybdate complex of acyclic L-sorbose (*Ve*) involves hydroxyl groups bound to carbon atoms C-3, C-4, C-5, and C-6 (Tables 1 and 2). In molybdate complex *Ve* hydroxyl groups are in *xylo* arrangement and <sup>13</sup>C NMR chemical shifts are in good accord with <sup>13</sup>C NMR data for the tetradentate binuclear molybdate complex of xylitol [11]. D-*gluco*-2-Heptulose (*VI*) along with the molybdate complex with cyclic structure (*VIa*) forms a molybdate complex with acyclic structure (*ca.* 5 %) as well. The signal of carbonyl group with the chemical shift  $\delta = 215.1$  proves that D-*gluco*-2-heptulose (*VI*) produces molybdate complex with acyclic structure. An assignment of other signals of the complex of this type could not be reliably carried out on the basis of spectral data. In the frame of the NMR study of the molybdate complexes of 2-ketoses we investigated also lactulose and dihydroxyacetone which did not reveal formation of molybdate complexes with ammonium molybdate.

In some cases for the purpose of identification of 2-ketoses it is suitable to compare their specific rotation values in water and in 4 % aqueous ammonium molybdate [1]. Difference between these two values of specific rotation is the greater, the greater is the portion of 2-ketose bound in the complex (Table 1). High negative value of specific rotation of D-tagatose and D-*manno*-2-heptulose measured in 4 % aqueous ammonium molybdate implies that these two 2-ketoses occur mainly in  $\beta$ -anomeric form (Table 3) that is in agreement with NMR data. Similarly, D-lyxose and D-mannose occur in the molybdate com-

Table 3

Specific rotation ( $[\alpha]_D^{20}(\rho = 0.8-1.1 \text{ g dm}^{-3})$ ) of some 2-ketoses and aldoses

Saccharide	In 4 % aqueous ammonium molybdate	In water
D-Tagatose	— 95	-- 4
D-Lyxose	— 59	— 14
D- <i>manno</i> -2-Heptulose	— 141	+ 29
D-Mannose	— 35	+ 14

plexes in  $\beta$ -anomeric form, their specific rotation values being close to those of D-tagatose and D-manno-2-heptulose (Table 3).

### Experimental

$^1\text{H}$  NMR spectra were measured using FT NMR spectrometer Bruker AM-300 (300.13 MHz) at the temperature 298 K in deuterium oxide. Mass ratio of ammonium molybdate and 2-ketose was 2:1. Sodium 3-(trimethylsilyl)propionate was used as an internal standard. Digital resolution was 0.12 Hz per point (Table 2).

$^{13}\text{C}$  NMR spectra (75.46 MHz) were measured with methanol ( $\delta = 50.15$ ) as internal standard with the pulse width 5  $\mu\text{s}$ , flip angle 25°, relaxation delay 2 s, acquisition time 0.98 s and digital resolution 1.6 Hz per point. Number of accumulations in the case of L-sorbose, D-gluco-2-heptulose, and lactulose was substantially higher than with other 2-ketoses (ca. 12 000) (Table 1).

Specific rotation of the aldoses and 2-ketoses was measured using Perkin—Elmer polarimeter, model 241 (Table 3).

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