Reactions of saccharides catalyzed by molybdate ions XXXIX.*NMR spectra of the aldoses of ribose and arabinose homomorphous series in molybdate complexes

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It was proved by means of NMR spectroscopy that in aqueous solutions D-ribose, D-talose, D-*glycero*-D-*talo*-heptose, and D-*glycero*-L-*talo*-heptose form with ammonium molybdate the molybdate complexes. In these complexes the saccharides are preferably in pyranoid structures, the conformation being preferably close to ***B*** and ***C***, and hydroxyl groups on carbon atoms C-2, C-3, and C-4 being involved in complexation. Aldoses belonging to the arabinose homomorphous series, D-arabinose, D-galactose, D-*glycero*-D-*galacto*-heptose, and D-*glycero*-L-*galacto*-heptose form in two conformations of acyclic structures binuclear tetradentate molybdate complexes preferably involving hydroxyl groups on carbon atoms C-2, C-3, C-4, and C-5. The octoses D-*erythro*-L-*talo*-octose and D-*erythro*-L-*galacto*-octose preferably produce molybdate complexes involving hydroxyl groups bound to carbon atoms C-5, C-6, C-7, and C-8 with the forced furanoid structures of the aldooctoses.

С помощью ЯМР спектроскопии показано, что в водных растворах D-рибоза, D-талоза, D-*глицеро*-D-*тало*-гептоза и D-*глицеро*-L-*тало*-гептоза образуют с молибденатом аммония молибдатные комплексы. В этих комплексах сахариды имеют предпочтительно пираноидную структуру с конформацией близкой ***B*** или ***C***, причем в комплексообразовании принимают участие гидроксильные группы на атомах углерода С-2, С-3, и С-4. Альдозы из гомоморфного ряда арабинозы, D-арабиноза, D-галактоза, D-*глицеро*-D-*галакто*-гептоза и D-*глицеро*-L-*галакто*-гептоза образуют в двух конформациях ациклической формы двухъядерные тетрадентатные молибдатные комплексы с предпочтительным участием гидроксильных групп на углеродных атомах С-2, С-3, С-4 и С-5. Октозы D-*эритро*-L-*тало*-октоза и D-*эритро*-L-*галакто*-октоза преимущественно образуют молибдатные комплексы, включающие гидроксильные группы на атомах углерода С-5, С-6, С-7 и С-8 с вынужденно фураноидной формой альдооктоз.

*For Part *XXXVIII* see Ref. [6].

By means of ^{1}H NMR [1] and ^{13}C NMR [2] spectroscopy investigations of the aqueous solutions of the complexes formed with ammonium molybdate by some aldopentoses, -hexoses, and -heptoses of lyxose homomorphous series were carried out. These aldoses join the molybdate complexes preferably in pyranoid form with the hydroxyl groups bound to the carbon atoms C-1, C-2, and C-3. Hemiacetal hydroxyl group as well as that one at C-2 in the molybdate complex are *cis*. D-*erythro*-L-*manno*-Octose joins the complex in furanoid form and the molybdate complex preferably forms at the acyclic part of the molecule [3]. Analysis of the ^{13}C NMR spectra [2] and of the values of specific rotation [4] of L-ribose, D-talose, and D-allose revealed that these aldoses play in the molybdate complexes a role of tridentate donors involving hydroxyl groups bound to the carbon atoms C-2, C-3, and C-4. *Geraldes et al.* investigated using NMR spectroscopy the molybdate complexes of D-mannose, D-lyxose, D-ribose, D--arabinose, D-galactose, D-xylose, and D-glucose, as well as their complexes with W(VI) and U(VI) [5]. They confirmed that in molybdate complexes D-mannose, D-lyxose, resp. D-ribose occur in the cyclic forms with the donor hydroxyl groups bound to the carbon atoms C-1, C-2, C-3 and C-2, C-3, C-4, respectively [5]. Concerning D-arabinose, D-galactose, D-xylose, and D-glucose (mole ratio aldose : Mo(VI) = 1 : 8, pH = 5.8) it was found that they formed weak bidentate molybdate complexes also in cyclic forms with the hydroxyl groups attached to the carbons C-1 and C-3 of the aldose [5]. The molybdate complexes of alditols were studied by means of NMR spectroscopy as well [6].

In this paper we deal with NMR study of the molybdate complexes of the aldoses of ribose homomorphous series, *i.e.* D-ribose (*I*), D-talose (*II*), D-*glycero*--D-*talo*-heptose (*III*), D-*glycero*-L-*talo*-heptose (*IV*), D-*erythro*-L-*talo*-octose (*V*), D-*threo*-L-*talo*-octose (*VI*), as well as those of the aldoses of arabinose homomorphous series, *i.e.* D-arabinose (*VII*), D-galactose (*VIII*), D-*glycero*-D-*galacto*--heptose (*IX*), D-*glycero*-L-*galacto*-heptose (*X*), D-*erythro*-L-*galacto*-octose (*XI*), and D-*threo*-L-*galacto*-octose (*XII*).

Analyses of ^{1}H and ^{13}C NMR spectra of aldopentoses, -hexoses, and -heptoses of ribose homomorphous series in molybdate complexes (Tables 1 and 2) show that these aldoses occur in the molybdate complexes in pyranoid form involving hydroxyl groups bound to carbon atoms C-2, C-3, and C-4. Long--range coupling constant value $^4J_{2,4} = 2.0$ Hz in ^{1}H NMR spectra of D-ribose and D-talose indicates the *W*-type orientation among the protons H-2 and H-4. Similar values of these coupling constants were observed for *talo*-heptoses *III* and *IV*. From the changes of optical rotation of the aldoses of ribose homomorphous series in molybdate solutions it can be deduced that the anomeric hydroxyl group is in *trans* position to the hydroxyl group at the carbon C-2 [4]. The atypical value of the coupling constant between protons H-1 and H-2 $J_{1,2} = 5.8$ Hz estimated for the β-anomer of D-ribose implies that D-ribose in

Table 1

^{13}C NMR data of the molybdate complexes of the aldoses of ribose homomorphous series

Aldose	Chemical shift/ppm							Aldose conformation in the complex	Ratio of complexes
	C-1	C-2	C-3	C-4	C-5	C-6	C-7		
I	102.8	80.5	86.5	76.3	66.5			$B_{1,4}$	$B_{1,4} : {}^1C_4 = 10 : 1$
	99.2	78.7	80.5	84.6	63.4			$^1C_4$	
II	103.8	80.5	87.1	76.7	[illegible]	64.4		$^{1,4}B$	$^{1,4}B : {}^4C_1 = 3 : 2$
	99.7	79.4	81.0	84.9	75.4	63.6		$^4C_1$	
III	103.1	80.3	87.2	76.2*	76.0*	71.5	64.2	$^{1,4}B$	$^{1,4}B : {}^4C_1 = 2 : 1$
	99.7	79.2	80.3	84.8	74.3	71.5	64.2	$^4C_1$	
IV	103.8	80.4	87.4	76.6	76.6	71.8	63.8	$B_{1,4}$	$B_{1,4} : {}^1C_4 = 4 : 3$
	99.7	79.3	81.0	84.8	75.0	71.8	63.5	$^1C_4$	

* Signals can be interchanged.

Table 2

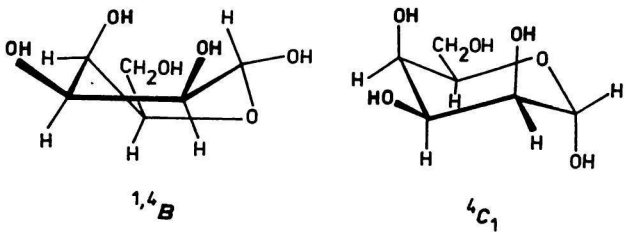
^{1}H NMR data of the molybdate complexes of the aldoses of ribose homomorphous series

Aldose	Chemical shift/ppm										Aldose conformation in the complex
	H-1	H-2	H-3	H-4	H-5	H-5′	H-6	H-6′	H-7	H-7′	
I	6.11	4.80	4.88	4.53	4.22	4.10					$\boldsymbol{B}_{1,4}$
II	6.15	4.83	4.87	4.61	4.08		4.16	3.97			$^{1,4}\boldsymbol{B}$
	5.63	4.93	5.03	4.93	*		*	*			$^4\boldsymbol{C}_1$
III	6.17	4.78	4.91	4.62	*		*		*	*	$^{1,4}\boldsymbol{B}$
	5.61	4.88	*	*	*		*		*	*	$^4\boldsymbol{C}_1$
IV	6.12	4.73	4.90	4.58	*		*		*	*	$\boldsymbol{B}_{1,4}$
	5.65	4.84	*	*	*		*		*	*	$^1\boldsymbol{C}_4$

Aldose	Coupling constants J/Hz							Aldose conformation in the complex
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	Other	$^4J_{2,4}$	
I	5.8	4.9	2.5	<0.2		$J_{4,5'}$ 5.7; $J_{5,5'}$ − 11.5	2.0	$\boldsymbol{B}_{1,4}$
II	5.8	4.8	2.2	4.2	8.2	$J_{5,6'}$ 4.2; $J_{6,6'}$ − 10.4	2.0	$^{1,4}\boldsymbol{B}$
	1.8	*	*	*	*	*	*	$^4\boldsymbol{C}_1$
III	6.0	*	2.2	4.4	*	*	2.1	$^{1,4}\boldsymbol{B}$
	1.8	*	*	*	*	*	*	$^4\boldsymbol{C}_1$
IV	6.1	*	2.2	4.5	*	*	2.1	$\boldsymbol{B}_{1,4}$
	1.8	*	*	*	*	*	*	$^1\boldsymbol{C}_4$

* Not assigned or not resolved.

molybdate complex preferably occurs in conformation close to $\boldsymbol{B}_{1,4}$. A similar situation is with D-talose (*II*) and *talo*-heptoses *III* resp. *IV*, which occur in molybdate complexes in α-anomeric form and the corresponding conformations close to $^{1,4}\boldsymbol{B}$ for *II* and *III* and $\boldsymbol{B}_{1,4}$ for *IV*. Along with the signals of this prevailing complex NMR spectra of *I*—*IV* contain the signals of an additional complex. On the basis of the values of coupling constants $J_{1,2} = 1.8$ Hz which are characteristic of diequatorial arrangement of the protons H-1 and H-2 and on the basis of chemical shift values of protons H-2, H-3, and H-4 estimated from the homocorrelated 2D NMR spectra (COSY-45) it can be suggested that in this case we deal with the complex with donor hydroxyl groups at the carbon atoms C-2, C-3, and C-4, having however conformation close to $^{1}\boldsymbol{C}_{4}$ for *I* and *IV*, or $^{4}\boldsymbol{C}_{1}$ for *II* and *III*. Conformations of D-talose in the molybdate complexes are demonstrated in Scheme 1.



Scheme 1

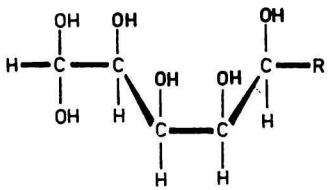
Conformations of α-D-*talo*-pyranose in the molybdate complexes are close to the conformation $^{1,4}\boldsymbol{B}$ and $^{4}\boldsymbol{C}_{1}$ (hydroxyl groups involved in molybdate complex are graphically emphasized).

Table 3

^{13}C NMR data of the molybdate complexes of the aldoses of arabinose homomorphous series

Aldose	Chemical shift/ppm							Complex type	Ratio of complexes
	C-1	C-2	C-3	C-4	C-5	C-6	C-7		
VII	92.3	81.6	82.7	91.7	70.3			A_1	$A_1 : A_2 = 3 : 2$
	90.5	84.8	91.5	83.0	72.8			A_2	
VIII	92.3	81.6	91.4	82.9	82.5	63.8		A_1	$A_1 : A_2 = 2 : 1$
	90.5	84.5	91.0	83.0	78.7	64.7		A_2	
IX	92.3	81.7	91.6	82.8	81.8	71.8	64.4	A_1	$A_1 : A_2 = 3 : 1$
	90.5	84.6	91.1	83.0	79.3	72.8	64.7	A_2	
X	92.3	81.5	91.5	82.8	82.4	74.2	63.8	A_1	$A_1 : A_2 = 3 : 2$
	90.5	84.6	91.1	83.1	79.6	75.2	63.5	A_2	

^{13}C and ^{1}H NMR spectra (Tables 3 and 4) of the acyclic form of the aldoses of arabinose homomorphous series in the part of the molecule involved in the complexation, are in good agreement with the ^{1}H and ^{13}C NMR spectra of corresponding alditols in molybdate complexes [6]. Alditols form binuclear complexes of four types involving four vicinal hydroxyl groups. In two of these types, the shape of the carbon chain remains close to zig-zag arrangement, whereas in two other types carbon chain is forced to a sickle arrangement [6]. In the case of arabinitol the complex is formed involving four vicinal hydroxyl groups attached to carbon atoms C-2, C-3, C-4, and C-5 (*arabino* configuration). This type of the complexes we designated as type *A* (Scheme 2) [6]. In ^{1}H NMR spectra of this complex of arabinitol characteristic splitting of H-5′ signal ($\delta = 4.07$) with the long-range coupling constant $^{4}J_{3,5'} = 2.0$ Hz is observed, as well as the coupling constant $^{3}J_{4,5} < 0.2$ Hz, which causes characteristic doublet splitting of H-5 signal ($\delta = 4.35$). For the preferable molybdate complex of arabinose the values of ^{1}H and ^{13}C NMR chemical shifts and of the coupling constants coincide well with the corresponding values for arabinitol in type *A* molybdate complex. That implies that D-arabinose occurs in this molybdate complex in acyclic form, and hence we will designate such binuclear tetradentate molybdate complex of D-arabinose also as type *A* complex. NMR spectra of D-arabinose molybdate complexes contain also the signals indicating the presence of additional aldose complex with acyclic structure.



Scheme 2

Acyclic structures of the aldoses of arabinose homomorphous series in molybdate complexes (hydroxyl groups involved in molybdate complex are graphically emphasized). R = H for arabinose, CH_2OH for galactose, and $CHOHCH_2OH$ for *galacto*-heptoses.

Theoretically it could be expected that this complex of the second type might involve in the formation of tetradentate binuclear molybdate complex the hydrated carbonyl group and hydroxyl groups bound to carbon atoms C-2, C-3, and C-4, with the carbon chain having an arrangement close to zig-zag. We found that in the case of D-xylose and D-glucose formation of tetradentate binuclear molybdate complex took place in which hydrated carbonyl group as well as three adjacent vicinal hydroxyl groups were involved, and the aldoses had acyclic structures with the carbon chain close to zig-zag arrangement.

Table 4

^{1}H NMR data of the molybdate complexes of the aldoses of arabinose homomorphous series

Aldose	Chemical shift/ppm										Complex type
	H-1	H-2	H-3	H-4	H-5	H-5′	H-6	H-6′	H-7	H-7′	
VII	5.07	4.17	4.90	4.76	4.34	4.07					A_1
	5.21	4.03	*	*	*	*					A_2
VIII	5.08	4.07	4.86	4.68	4.53		3.87	3.75			A_1
	5.21	4.17	4.76	4.93	4.35		3.70	3.70			A_2
IX	5.08	4.02	4.88	4.99	4.28		3.97		3.68	3.63	A_1
	5.23	4.16	4.91	4.96	*		*	*			A_2
X	5.08	4.04	**	**	4.42		3.90		3.75	3.60	A_1
	5.21	4.16	**	**	4.27		3.87		3.75	3.60	A_2

Aldose	Coupling constants J/Hz							Complex type
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	Other	
VII	7.3	<0.2	4.4	<0.2			$J_{4,5'}$ 2.3; $J_{5,5'}$ − 10.3; $^4J_{3,5'}$ 2.0	A_1
	7.3	*	*	*			*	A_2
VIII	7.5	<0.2	4.6	<0.2	8.1		$J_{5,6'}$ 5.8; $J_{6,6'}$ − 11.6	A_1
	7.5	<0.2	4.6	<0.2	6.9		$J_{5,6'}$ 6.9; $J_{6,6'}$*	A_2
IX	7.3	<0.2	4.3	<0.2	9.0	6.6	$J_{6,7'}$ 5.7; $J_{7,7'}$ − 12.3	A_1
	7.6	<0.2	4.3	<0.2	8.3		*	A_2
X	7.2	<0.2	*	*	*	*	*	A_1
	7.4	<0.2	*	*	*	*	*	A_2

* Not assigned; ** Signals are overlapped in the range 4.75–4.95 ppm.

Molybdate complexes of these aldoses are the item of our further studies. For D-xylose or D-glucose in the molybdate complex the observed value of the chemical shift of C-1 carbon of the hydrated carbonyl group was 99.7 ppm and the chemical shift value of H-1 was 5.44 ppm (D-xylose) or 5.48 ppm (D--glucose). These results point out that it is necessary to re-estimate the structures of the molybdate complexes of the aldoses which can be in cyclic structures exclusively in furanoid form (D-erythrose, 5-deoxy-L-ribose, D-threose, 5-deoxy--L-arabinose) [7]. The named aldoses occur in molybdate complexes not in cyclic, but in acyclic structures in which a role of donor hydroxyl groups is played by the hydrated carbonyl group and three vicinal hydroxyl groups at the carbon atoms C-2, C-3, and C-4. The chemical shift value of C-1 carbon with the hydrated carbonyl group involved in complexation was 99.6 ppm for D-threose and 99.8 ppm for 5-deoxy-L-arabinose. For 5-deoxyaldopentoses and 5-*O*--methylaldopentoses which can adopt cyclic structures only in furanoid forms also acyclic aldehydrol and aldehyde forms were detected in aqueous solutions [8].

The chemical shift value of C-1 carbon of the hydrated carbonyl group of the aldoses lies in the range 90.0—91.8 ppm, and that of H-1 proton in the range 5.01—5.17 ppm [8—10]. The analysis of these results implies that the chemical shift values of the hydrated form of the molybdate D-arabinose complex of the second type (for C-1 $\delta = 90.5$ and for H-1 $\delta = 5.21$) do not mean that this hydrated form is involved into the formation of the molybdate complex. Besides that, the shift of C-5 carbon signal to the lower magnetic field ($\delta = 72.8$) testifies that the primary hydroxyl group is involved in the complexation. All these facts mean that the type *A* complex exists as two conformers which we will designate as complexes of type A_1 and type A_2 (Tables 3 and 4).

In the case of galactitol an extremely stable molybdate complex is formed with the participation of all four secondary hydroxyl groups of the galactitol arrangement. The complex of this type has its carbon chain in the sickle shape and from this point of view is similar to D-arabinose molybdate complex (Scheme 2) [6].

From the analysis of ^{1}H and ^{13}C NMR spectra it follows that aldoses *VIII*, *IX*, and *X* form the molybdate complexes with acyclic structures and these are analogous to those of galactitol, but having two different conformations which we will designate as type A_1 and type A_2 complexes. NMR data of the preferable type A_1 complex are in good agreement with those of galactitol molybdate complex [6]. In the molybdate complexes of *VIII*, *IX*, and *X* the values of ^{1}H and ^{13}C NMR chemical shifts of the hydrated carbonyl group coincide well with those of the hydrated carbonyl group of D-arabinose in molybdate complex (Tables 3 and 4). In these spectra chemical shift values of the carbon atoms bearing primary or secondary hydroxyl groups not involved in the molybdate

complex of *VIII*, *IX*, and *X* do not significantly differ from those of the corresponding alditols measured in the aqueous solutions. That implies that the donor hydroxyl groups are attached to the carbon atoms C-2, C-3, C-4, and C-5 of the type A_1 conformer as well as of the type A_2 one. Coupling constants values in ^{1}H NMR spectra of both conformers are in good concordance in the site of complexation (Table 4). Simultaneously it means that the conformers differ from each other in the spatial orientation only of those parts of aldose molecule which are not involved in complexation (Scheme 2).

From the total content of the molybdate complexes of both types A_1 and A_2 in the case of D-galactose (30 %) approximately 5 % represents molybdate complex with nonhydrated carbonyl group. The presence of this form is proved in ^{1}H NMR spectra by the signal of aldehyde form proton with $\delta = 9.77$ and the signal with $\delta = 209.8$ in ^{13}C NMR spectra.

The value of single-bond coupling constant $^1J_{C\text{-}1,H\text{-}1}$ for D-galactose is 166.3 Hz for A_1 conformer and 162.0 Hz for A_2 conformer. In aqueous solutions the corresponding values for the acyclic hydrated forms of D-threose and D-erythrose are 162.8 Hz and 164.2 Hz, respectively [11]. In the NMR spectra of *VIII* along with the signals of the preferred molybdate complexes of A_1 type and A_2 type, the signals were observed which indicated the presence of the additional type of molybdate complex (1—2 %). This complex is displayed in ^{1}H NMR spectrum by the signal with $\delta = 5.37$ ($J_{1,2} = 4.4$ Hz) and also by the signals in ^{13}C NMR spectrum which however could not be unambiguously assigned. In this case apparently the complex is formed that involves hydrated carbonyl group as well as hydroxyl groups bound to carbon atoms C-2, C-3, and C-4. The applied technique of homocorrelated 2D-spectroscopy COSYLR with the expressed long-range couplings as well as semiselective INEPT experiment confirmed that aldoses *VII*—*X* in molybdate complexes have acyclic structures.

Aldooctoses in aqueous solutions have preferably pyranoid structures [3, 12]. D-*erythro*-L-*manno*-Octose and D-*erythro*-L-*gluco*-octose transform into furanoid forms as a result of the formation of preferable tetradentate molybdate complex in the acyclic part of the molecule (*arabino* configuration) [3]. In the case of D-*erythro*-L-*talo*-octose (*V*) and D-*erythro*-L-*galacto*-octose (*XI*), preferable formation of the molybdate complex that involves hydroxyl groups at the carbon atoms C-5, C-6, C-7, and C-8 (*arabino* configuration) also takes place. The following values of the chemical shifts are characteristic of the complex of this type. For the carbons C-5 and C-6 $\delta \approx 83$, for C-7 $\delta \approx 91.5$ and for C-8 $\delta \approx 70$. Together with the complex of this type with furanoid structures of aldooctoses *V* and *XI*, complexes of other types are also formed in a significant amount, which we were not able to identify more precisely on the basis of spectral data. These are probably the complexes of acyclic structures of aldooctoses. NMR spectra of the molybdate complexes of D-*threo*-L-*talo*-octose (*VI*)

and D-*threo*-L-*galacto*-octose (*XII*) are very complex and due to this fact they cannot be reliably analyzed. On the basis of the results of our NMR study of the molybdate complexes of the aldoses, 2-ketoses, and alditols it can be concluded that *VI* and *XII* occur in the molybdate complexes in acyclic as well as cyclic forms. In the case of molybdate complexes of *XII* we were able to detect reliably only the presence of type A_1 complex in which hydroxyl groups bound to the carbon atoms C-2, C-3, C-4, and C-5 of the acyclic structure of *XII* were involved. The chemical shift values of the carbons in the complex of this type (δ/ppm for C-1 to C-5, respectively: 92.4, 81.7, 91.3, 82.9, and 82.6) were in good accord with the data determined for type A_1 complex of *VIII*—*X* (Table 3). Essentially more complicated is evaluation of NMR spectra of the molybdate complexes of *VI*. In this case probably occur molybdate complexes of both acyclic and cyclic structures.

The readiness to formation of the molybdate complexes is different for different aldoses. Among aldoses *I*—*IV* of ribose homomorphous series at the used experimental conditions, the amount of the aldose involved in complexation reaches about 40 % of the total amount of aldose. In arabinose homomorphous series the ratio of complexed and noncomplexed aldose varies in greater degree. In the molybdate complexes the amount of complexed D-arabinose is 10 %, that of D-galactose and D-*glycero*-L-*galacto*-heptose is 30 %, and of D-*glycero*-D-*galacto*-heptose 40 %. The best complexation ability is exhibited by aldooctoses (50 % for *XII*, 60 % for *XI* and 70 % for *VI*) and especially by D-*erythro*-L-*talo*-octose (90 %). We investigated also the formation of molybdate complexes of D-ribose and D-galactose in dependence upon the temperature. At the temperatures 25 °C and 60 °C for these D-aldoses no significant differences were observed in the ratio of the formed molybdate complexes and their total amount.

Experimental

For NMR measurements aqueous solutions containing aldose and ammonium molybdate in the mass ratio 1 : 2 at pH = 5.6—5.8 were used. For pH measurements Standard pH-Meter PHM-82 (Radiometer, Copenhagen) was used.

^{1}H NMR spectra were measured using FT NMR spectrometer Bruker AM-300 (300.13 MHz) at the temperature 298 K in deuterium oxide. Sodium 3-(trimethylsilyl)-propionate was used as an internal standard. Digital resolution was 0.12 Hz per point.

^{13}C NMR spectra (75.46 MHz) were measured at the same conditions as ^{1}H NMR spectra with methanol (δ = 50.15 ppm) as internal standard. Digital resolution was 1.6 Hz per point.

An assignment of the signals in NMR spectra was carried out using the following

techniques of homocorrelated COSY-45, COSYLR, heterocorrelated CH HETCORR, RELAY, homonuclear *J*-resolved spectroscopy and semiselective INEPT. COSYLR experiment was optimalized according to the long-range constant of the value $^{l,r}J_{H,H} = 1.25$ Hz.

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