Reactions of saccharides catalyzed by molybdate ions XXXVIII.* NMR spectra of alditols in molybdate complexes

M. MATULOVÁ, V. BÍLIK, and J. ALFÖLDI

Institute of Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, CS-842 38 Bratislava

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The formation of complexes of 17 selected alditols with ammonium molybdate in aqueous solutions was investigated by ^{1}H and ^{13}C NMR spectroscopy. Alditols form four types of binuclear molybdate complexes in which they serve as tetradentate donors with four vicinal hydroxyl groups. In two types of alditol-molybdate complexes the alditol carbon chain remains in the shape close to a zig-zag arrangement. In other two types of complexes the alditol carbon chain is forced to a sickle arrangement.

С помощью ^{1}H и ^{13}C ЯМР спектроскопии изучено комплексообразование 17 избранных альдитолей с молибдатом аммония в водных растворах. Альдитоли образуют двухъядерные молибдатные комплексы четырех типов, в которых они играют роль тетрадентатных доноров с четырьмя вицинальными гидроксильными группами. В альдитоль-молибдатных комплексах двух типов углеродная цепь альдитоля сохраняет форму близкую зигзагообразной. В комплексах двух других типов углеродная цепь альдитоля вынуждена принять серпообразную форму.

The formation of molybdate complexes of alditols in aqueous solutions was documented by polarimetry [1—3], electrophoresis [4, 5], and acidometry [6, 7]. NMR spectroscopy was used to follow the complexation of alditols with Eu^{3+} [8—10], Pr^{3+} [10, 11], La^{3+} and Yb^{3+} [10] ions. Due to a great flexibility of the carbon chain, alditols occur as several conformers [12—16] and, consequently, they offer multiple types of arrangements of hydroxyl groups suitable for complex formation. Complexes of alditols with molybdate ions have not been studied yet by NMR spectroscopy. Such studies carried out with aldoses pointed out, however, that some aldoses complex with molybdate in cyclic structures as tridentate donors [17—20].

NMR spectra of alditols in aqueous media [12—16] considerably differ from

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those recorded in the presence of molybdate. The formation of the molybdate complexes of aldoses can be established by NMR spectroscopy from changes in the chemical shifts caused by deshielding effect of the molybdenum nucleus and by nonbonding interactions, and from changes in the coupling constants $J_{H,H}$ [17—20].

The assignment of signals in NMR spectra was done by homocorrelated (COSY-45) [21], heterocorrelated (HETCORR, RELAY) [22, 23], and homonuclear *J*-resolved spectroscopy [24] as well as by semiselective INEPT [25].

A comparison of ^1H and ^{13}C NMR spectra of erythritol (*I*) in water and aqueous solution of ammonium molybdate showed unambiguously the formation of a molybdate complex of erythritol (Tables 1—3). Changes in chemical shifts were observed in both ^1H NMR spectra ($\approx +1$ ppm) and ^{13}C NMR spectra ($\approx +10$ ppm). The long-range coupling constant $^4J = 2.0$ Hz indicated a planar arrangement of the carbon chain and a simultaneous W-type orientation between the proton H-4′ ($\delta = 4.05$ ppm) and proton H-2 ($\delta = 4.83$ ppm).

In the case of glycerol and 2-deoxy-D-*erythro*-pentitol ^1H and ^{13}C NMR spectra recorded in water and aqueous solution of ammonium molybdate were identical. This means that four vicinal hydroxyl groups are prerequisite for complex formation with molybdate.

L-Arabinitol (*II*) forms with molybdate two types of complexes. One complex involves four hydroxyl groups at carbon atoms C-2, C-3, C-4, and C-5 (the *arabino* configuration) which exhibit the greatest changes in chemical shifts (Table 1). The secondary hydroxyl groups at carbon atoms C-3 and C-4 next to the primary hydroxyl group at carbon atom C-5 are in the *erythro* configuration. This type of complexes shows a long-range coupling constant $^4J_{3,5'} = 2.0$ Hz evident on the proton H-5′ ($\delta = 4.07$ ppm) as well as a doublet splitting of the proton H-5 ($\delta = 4.35$ ppm) (Tables 2 and 3). The primary hydroxyl group at carbon atom C-5 occurs in a *gauche* orientation towards the vicinal secondary hydroxyl group. In this type of complexes the left *gauche* orientation of the vicinal hydroxyl groups is alternated by the right *gauche* orientation [12]. Such complexes are described as complexes of type *A* (Scheme 1). From the spectral data it was not possible to determine reliably the second type of the molybdate complex of L-arabinitol.

NMR data showed that 5-deoxy-D-arabinitol (*III*) forms with molybdate the *B*-type complex. The assignment of chemical shifts and coupling constants of L-arabinitol and its molybdate complex was based on ^1H NMR data of D-[3-^{2}H]arabinitol. Ribitol (*IV*) forms with molybdate the *A*-type complex that involves all secondary and one primary hydroxyl groups, as confirmed by the presence of a long-range coupling on the H-5′ ($\delta = 4.02$ ppm) (Tables 2 and 3). Xylitol (*V*) forms with molybdate a *B*-type complex by means of three secondary hydroxyl groups (the *xylo* configuration) and one primary hydroxyl

group. The *B*-type complex containing the *xylo* configuration shows in ^{13}C NMR spectrum larger halfwidths of signals and in ^{1}H NMR spectrum broad signals that do not enable the spectrum interpretation.

Analysis of NMR spectra of D-glucitol (*VI*) pointed out that preferred molybdate complexes of type *A* and type *B* are formed in the ratio 1 : 3. The spectra also contain signals indicating the presence of additional type of the complex, the structure of which could not be unambiguously ascertained from the spectral data. Chemical shifts in NMR spectra of D-glucitol were assigned on the basis of the spectra of 6-deoxy-L-glucitol (*VII*) and 2-deoxy-D-*arabino*--hexitol (*VIII*). Compound *VIII* forms the *A*-type complex. Compound *VII* forms the *B*-type complex together with additional complex described as type *D* (Scheme 1). The *D*-type complex involves four vicinal secondary hydroxyl groups of the alditol with carbon chain being close to a zig-zag arrangement.

In further, the effect of molybdate on periodate oxidation of D-glucitol was investigated. Xylose was the predominant product formed in the absence of molybdate, while equal amounts of xylose and arabinose were obtained in the presence of molybdate (Table 4). The difference in the amount of arabinose serves as an evidence that the hydroxyl groups on carbon atoms C-3—C-6 are protected against periodate oxidation in the molybdate complex of type *A*, which was actually demonstrated by NMR spectroscopy. The aqueous solution of ammonium molybdate also contains considerable portion of the starting D-glucitol. This observation suggests that the unidentified molybdate complex involves all secondary hydroxyl groups and is the *D*-type complex. D-Mannitol (*IX*) and 1-deoxy-L-mannitol (*X*), similarly as *VIII*, form only the *A*-type molybdate complexes. Periodate oxidation of *IX* in aqueous solution gives 35 % of arabinose, small amount of erythrose, and other lower oxidation products. Periodate oxidation of *IX* in aqueous solution of ammonium molybdate gives arabinose as the main product ($\approx$ 90 %). From these results one may conclude that during oxidative cleavage of *IX* the primary hydroxyl group and the adjacent secondary hydroxyl group are free while other hydroxyl groups are protected in the molybdate complex. X-Ray analysis of the complex of D--mannitol with sodium molybdate (Na_2MoO_4 $2H_2O$) has established that D--mannitol enters a binuclear molybdate complex with three vicinal secondary hydroxyl groups and the adjacent primary hydroxyl group [26].

Galactitol (*XI*) and D-altritol (*XII*) molybdate complexes involve all four secondary hydroxyl groups. In such complexes, designated as the *C*-type complexes (Scheme 1) the alditol carbon chain is arranged to a sickle shape. ^{1}H and ^{13}C NMR spectra of *XI* and *XII* measured in the solution of ammonium molybdate do not show any changes of chemical shifts of primary protons and their carbons, which suggests that they do not take part in the complex formation. Periodate oxidation of *XI* in water gives $\approx$ 35 % of lyxose besides threose

Table 1

^{13}C NMR data of alditols

Alditol	Chemical shift δ/ppm							Complex type	Ratio of complexes
	C-1	C-2	C-3	C-4	C-5	C-6	C-7		
I *a*	63.9	73.2	73.2	63.9					
b	73.2	82.7	91.7	70.2				*A*	
II *a*	64.2	71.5	71.7	72.2	64.3				
b	63.8	82.8	82.9	91.5	70.2			*A*	
III *a*	64.3	71.9	75.8	68.3	19.4				
b	76.4	77.5	85.7	81.0	16.8			*B*	
IV *a*	63.6	73.3	73.4	73.3	63.6				
b	63.0	86.7	82.8	89.9	71.0			*A*	
V *a*	63.9	73.2	72.0	73.2	63.9				
b	76.1	83.4*	82.5*	85.7*	63.9			*B*	
VI *a*	63.8	74.3	71.0	72.6	72.5	64.2			
b	63.9	74.2	82.8	82.7	91.7	70.1		*A*	$A:B = 1:3$
b	76.1	83.3*	82.2*	84.8*	71.1	64.4		*B*	
VII *a*	64.4	72.2	70.6	74.5	68.3	20.2			
b	76.1	83.4*	82.2*	89.5*	67.1	20.5		*B*	$B:D = 1:2$
b	63.2	77.2	81.0	85.8	86.5	16.8		*D*	

Table 1 (Continued)

Alditol		Chemical shift δ/ppm							Complex type	Ratio of complexes
		C-1	C-2	C-3	C-4	C-5	C-6	C-7		
VIII	*a*	59.8	36.5	68.1	74.3	72.3	64.3			
	b	60.0	37.1	79.7	86.0	91.7	70.1		*A*	
IX	*a*	64.5	72.1	70.5	70.5	72.1	64.5			
	b	64.4	71.7	82.0	82.8	91.8	70.1		*A*	
X	*a*	20.2	68.3	74.5	70.6	72.2	64.4			
	b	20.5	68.3	86.3	82.9	91.8	70.2		*A*	
XI	*a*	64.5	71.5	70.7	70.7	71.5	64.5			
	b	64.9	78.7	91.0	82.9	82.6	64.0		*C*	
XII	*a*	64.2	71.7	71.9	72.7	73.8	63.3			
	b	64.6*	79.2	89.2	82.8	86.5	62.9*		*C*	
XIII	*a*	64.6	71.5	70.5	69.5	70.4	72.2	64.6		
	b	64.7	78.7	91.1	82.8	81.8	71.8	64.4	*C*	$C:D = 2:1$
	b	64.7*	72.8	79.2	91.1	83.0	82.6	63.8*	*D*	
XIV	*a*	64.5	72.1	70.9	71.0	72.8	74.1	63.4		
	b	70.2	91.7	83.2	82.0	71.6	74.4	62.8	*A*	$A:C = 2:1$
	b	63.0*	73.0	79.8	89.4	82.9	86.6	64.6*	*C*	

a) Aqueous solution of alditol; *b*) alditol in aqueous solution of ammonium molybdate.
* The chemical shifts can be interchanged.

Table 2

Chemical shifts of protons (δ/ppm) in ^{1}H NMR spectra of alditols

Alditol		Ref.	H-1	H-1′	H-2	H-3	H-4	H-4′	H-5	H-5′	H-6	H-6′	H-7	H-7′	CH_3	Complex type
I	*a*	[12]	3.77	3.62	3.665											
	b		4.52	4.52	4.83	4.74	4.29	4.05								*A*
II	*a*	[12]	3.675	3.66	3.93	3.57	3.75		3.84	3.65						
	b		3.88	3.73	4.54	4.65	4.75		4.35	4.07						*A*
III	*a*		*	*	*	3.48	*								1.23	
	b		4.18	4.18	4.60	4.20	4.46								1.38	*B*
IV	*a*	[12]	3.80	3.65	3.815	3.69										
	b		*	*	4.83	4.72	4.80		4.40	4.02						*A*
V	*a*	[12]	3.715	3.64	3.80	3.64										
	b		broad lines													*B*
VI	*a*	[12]	3.73	3.62	3.84	3.85	3.65		3.77		3.83	3.65				
	b		*	*	*	*	*		*		4.33	4.05				*A*
VII	*a*		3.72	3.62	3.80	3.79	3.52		3.90						1.22	
	b		broad lines													*B*

Table 2 (Continued)

Alditol		Ref.	H-1	H-1′	H-2	H-3	H-4	H-4′	H-5	H-5′	H-6	H-6′	H-7	H-7′	CH_3	Complex type
VIII	*a*		3.75	3.75	1.80	4.02	3.44		3.75		3.84	3.66				
	b		3.74	3.74	1.86	4.67	4.60		4.75		4.34	4.05				*A*
IX	*a*	[12]	3.86	3.67	3.75	3.79										
	b		3.83	3.60	3.98	4.29	4.95		4.76		4.32	4.07				*A*
X	*a*	[13]			3.88	3.61	3.80		3.76		3.87	3.68			1.29	
	b				4.09	4.05	4.93		4.75		4.32	4.07			1.28	*A*
XI	*a*	[12]	3.71	3.71	3.99	3.69										
	b		3.71	3.71	4.36	4.75	4.68		4.54		3.87	3.73				*C*
XII	*a*	[12]	3.66	3.66	3.94	3.66	3.79		3.92		3.80	3.67				
	b		3.68	3.68	4.82	4.78	4.78		4.43		3.68	3.68				*C*
XIII	*a*	[14]	3.69	3.69	3.98	3.67	3.92		3.81		3.77		3.87	3.67		
	b		3.70	3.70	4.32	4.75	4.98		4.27		3.98		3.83	3.60		*C*
	b		*	*	*	4.19	4.89		4.70		4.52		*	*		*D*
XIV	*a*	[14]	3.85	3.66	3.74	3.78	3.89		3.80		3.94		3.81	3.68		
	b		4.05	4.28	4.72	4.90	4.34		*		*		*	*		*A*

a) and *b*) as in Table 1.
* Nonresolved signals.

Table 3

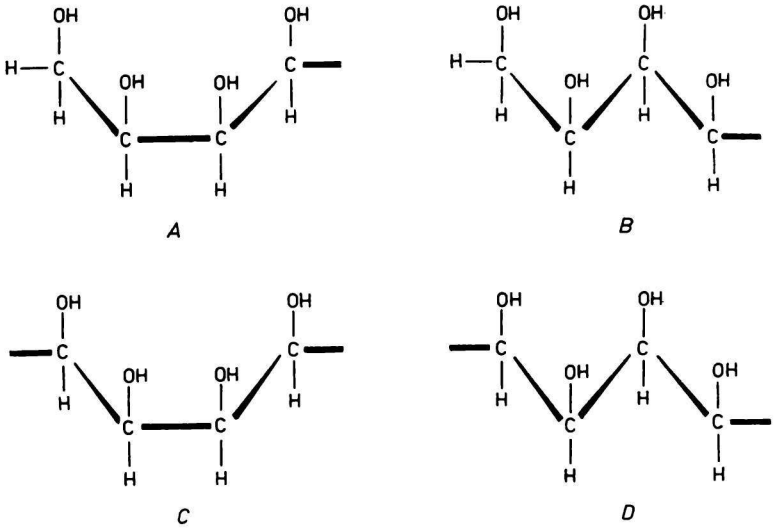
Coupling constants (J/Hz) in ^{1}H NMR spectra of alditols

Alditol		Ref.	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	Others	Complex type
I	*a*	[12]	−12.0	3.25	6.5	7.0						
	b		*	*	*	4.5	<0.2				$J_{3,4'}$ 2.7; $J_{4,4'}$ − 10.2; $^4J_{2,4'}$ 2.0	*A*
II	*a*	[12]	−11.55	5.0	7.55	2.0	8.4	3.05			$J_{4,5'}$ 6.5; $J_{5,5'}$ − 12.0	
	b		−11.2	8.2	5.3	0.8	4.4	<0.2			$J_{4,5'}$ 2.6; $J_{5,5'}$ − 10.3; $^4J_{3,5'}$ 2.0	*A*
III	*a*		*	*	*	3.0	6.4	6.5				
	b		*	*	1.8	*	*	6.7				*B*
IV	*a*	[12]	−12.0	3.0	7.25	6.25						
	b		*	4.3	7.6	3.9	3.9	<0.2			$J_{4,5'}$ 2.6; $J_{5,5'}$ − 10.2; $^4J_{3,5'}$ 2.0	*A*
V	*a*	[12]	−11.7	4.45	6.75	4.35						
	b		broad lines									*B*
VI	*a*	[12]	−12.0	3.55	6.55	6.0	1.7	8.25	2.95		$J_{5,6'}$ 6.3; $J_{6,6'}$ − 11.8	
	b		−11.8	3.6	6.8	*	*	*	<0.2		$J_{5,6'}$ 2.9; $J_{6,6'}$ − 10.3; $^4J_{4,6'}$ 2.0	*A*
VII	*a*		−11.5	4.4	6.6	5.7	3.5	7.0	6.6			
	b		broad lines									*B*
VIII	*a*		*	*	*	9.2	2.1	8.3	2.9		$J_{5,6'}$ 6.2; $J_{6,6'}$ − 11.4	
	b		*	*	*	9.6	4.1	4.1	<0.2		$J_{5,6'}$ 2.4; $J_{6,6'}$ − 10.2; $^4J_{4,6'}$ 2.0	*A*

Table 3 (Continued)

Alditol		Ref.	$J_{1,1'}$	$J_{1,2}$	$J_{1',}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	Others	Complex type
IX	*a*	[12]	−11.75	3.0	6.25	8.95	0.0					
	b		−11.7	2.7	6.8	9.5	0.0	4.1	<0.2		$J_{5,6'}$ 2.7; $J_{6,6'}$ − 10.1; $^4J_{4,6'}$ 2.0	*A*
X	*a*	[13]		6.3		7.8	1.5	8.5	2.6		$J_{5,6'}$ 6.0; $J_{6,6'}$ − 11.8	
	b			5.9		8.7	<0.2	4.2	<0.2		$J_{5,6'}$ 2.5; $J_{6,6'}$ − 10.2; $^4J_{4,6'}$ 2.0	*A*
XI	*a*	[12]	−11.5	5.4	7.4	1.5	9.4					
	b		*	6.7	6.7	<0.2	4.5	<0.2	8.3		$J_{5,6'}$ 5.4; $J_{6,6'}$ − 11.4	*C*
XII	*a*	[12]	−11.75	3.0	7.3	4.8	8.25	5.0	3.15		$J_{5,6'}$ 7.4; $J_{6,6'}$ − 12.0	
	b		*	*	*	*	*	<0.2	7.2		$J_{5,6'}$ 6.5; $J_{6,6'}$ − 10.7	*C*
XIII	*a*	[14]	−11.7	5.4	7.4	1.5	9.4	1.2	8.8	2.9	$J_{6,7'}$ 6.3; $J_{7,7'}$ − 11.7	
	b		*	*	*	<0.2	4.5	<0.2	9.2	2.9	$J_{6,7'}$ 6.7; $J_{7,7'}$ − 11.9	*C*
	b		*	*	*	8.5	<0.2	4.5	<0.2	*	$J_{6,7'}$ *; $J_{7,7'}$ *	*D*
XIV	*a*	[14]	−11.8	2.9	6.4	8.8	1.1	8.6	4.7	3.1	$J_{6,7'}$ 7.6; $J_{7,7'}$ − 11.8	
	b		−10.3	<0.2	2.7	4.3	<0.2	9.4	*	*	$J_{6,7'}$ *; $J_{7,7'}$ *; $^4J_{1',3}$ 2.0	*A*

a) and *b*) as in Table 1.
* As in Table 2.



Scheme 1

Configuration of the donor vicinal hydroxyl groups suitable for formation of four types of complexes with molybdate.

Table 4

Periodate oxidation of alditols

Alditol		Mole fraction x						
		Arabinose	Xylose	Lyxose	Ribose	Mannose	Altrose	Galactose
VI	*a*	0.16	0.33	—	—	—	—	—
	b	0.29	0.30	—	—	—	—	—
IX	*a*	0.35	—	—	—	—	—	—
	b	0.88	—	—	—	—	—	—
XI	*a*	—	—	0.34	—	—	—	—
	b	—	—	0.10	—	—	—	—
XII	*a*	—	—	0.45	0.36	—	—	—
	b	—	—	0.31	0.16	—	—	—
XIII	*a*	0.35	—	0.15	—	traces	—	0.16
	b	0.11	—	0.15	—	traces	—	0.59
XIV	*a*	0.21	—	—	0.33	0.11	0.15	—
	b	0.18	—	—	0.13	0.15	0.20	—

a) Aqueous solution of alditol; *b*) alditol in aqueous solution of ammonium molybdate.

and lower oxidation products. The same treatment of *XI* in the presence of ammonium molybdate gives 10 % of lyxose while almost 90 % of galactitol remains intact. Hence, the *C*-type complex of *XI* appears to be extremely stable. Although *XII* also forms the *C*-type complex, the results of periodate oxidation indicated its lower stability in comparison with *XI* (Table 4).

Perseitol (D-*glycero*-D-*galacto*-heptitol) (*XIII*) forms with molybdate two types of complexes. The preferred one involves the hydroxyl groups of the *galacto* configuration (type *C*) and the minor one the hydroxyl groups of the *manno* configuration (type *D*). The ratio of the *C*- and *D*-type complexes is 2 : 1. Periodate oxidation of *XIII* showed a higher stability of the complex of type *C* since in the presence of molybdate $\approx$ 60 % of galactose was formed. Volemitol (D-*glycero*-D-*manno*-heptitol) (*XIV*) forms three types of complexes with molybdate. The complex involving the hydroxyl groups at carbon atoms C-4—C-7 (type *A*) predominates. The hydroxyl groups at carbon atoms C-2—C-5 (the *talo* configuration) represent the donors in the second complex (type *C*). The ratio of complexes of type *A* and type *C* is 2 : 1. The ^{1}H and ^{13}C NMR spectra also contained signals indicating the existence of additional type of complex, however, the NMR data were insufficient for deducing its structure. The occurrence of multiple types of complexes of *XIV* is the main reason why the NMR data do not correlate with the results of periodate oxidation.

It can be concluded that alditols form with ammonium molybdate four types of complexes (*A*, *B*, *C*, and *D*) that involve interaction with four vicinal hydroxyl groups. In complexes of type *B* and *D* the alditol carbon chain occurs in the shape close to a zig-zag arrangement. In complexes of type *A* and *C* the alditol carbon chain is forced to a sickle arrangement. With alditols forming complexes in both arrangements of the carbon chain, the sickle type complexes predominate at 25 °C. At an increased temperature (70—80 °C) the proportion of molybdate complexes with sickle and zig-zag arrangement of the carbon chain of alditol becomes similar. The effect of temperature, stability of complexes and their ^{95}Mo NMR spectra are under current study.

Experimental

NMR spectroscopy

^{1}H NMR spectra were measured on an FT NMR spectrometer Bruker AM-300 (300.13 MHz) at a temperature of 295 K in deuterium oxide. The mass ratio of ammonium molybdate and alditol was 2 : 1. Sodium 3-(trimethylsilyl)propionate was used as internal standard. Digital resolution was 0.12 Hz per point.

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

Periodate oxidation of alditols

An aqueous solution (5 cm^3) of alditol (2.5 mmol) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}$ $4H_2O$) (0.75 mmol) was suddenly mixed with 10 cm^3 of aqueous solution of sodium periodate (5 mmol) and the mixture was left to stand at room temperature for 2 h. After addition of methanol (35 cm^3) and further 2 h standing the mixture was filtered and the filtrate made to 50 cm^3 volume with water. A part of this solution was chromatographed together with standard amounts of aldoses on Whatman No. 1 paper in 2-butanol—1-butanol—water ($\varphi_r = 16:2:1$) at room temperature for 20—40 h. After detection of the chromatograms with the anilinium hydrogen phthalate reagent, the colour areas were cut out, eluted with water and the absorbance of the eluates measured at $\lambda = 320$ nm. A similar procedure was applied for periodate oxidation of alditols in the absence of ammonium molybdate (Table 4).

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