ELSEVIER

Carbohydrate Research 277 (1995) 39–50

CARBOHYDRATE RESEARCH

Tungstate complexes of aldoses and ketoses of the *lyxo* series. Multinuclear NMR evidence for chelation by one or two oxygen atoms borne by the side chain of the furanose ring ☆

Stella Chapelle [a,*], Jean-François Verchère [b]

[a] *Université de Rouen, Laboratoire de RMN, URA 464 du CNRS, Faculté des Sciences, F-76821 Mont-Saint-Aignan, France*

[b] *Université de Rouen, URA 500 du CNRS, Faculté des Sciences, F-76821 Mont-Saint-Aignan, France*

Received 22 March 1995; accepted 30 May 1995

Abstract

The formation of tungstate complexes of aldoses and ketoses with *lyxo* configuration was studied in aqueous solution by ^{13}C and ^{183}W NMR spectroscopy. Two series of complexes were structurally characterized, in which the sugars adopt the furanose form and chelate a ditungstate group at a tetradentate site. All sugars form a major complex (type L for *lyxo*) similar to the molybdate species, in which the sites of chelation, O-1,2,3,5 for aldoses or O-2,3,4,6 for ketoses, involve the anomeric oxygen atom and the side chain atom O-5 or O-6. A second type of complex was identified (type M for *manno*), in which the sites of chelation are O-2,3,5,6 for D-mannose (tungstate species only) and O-3,4,6,7 for D-*manno*-heptulose (tungstate and molybdate complexes). The overall equilibrium constants for the formation of the complexes are reported and show that ketoses form stronger complexes than aldoses.

Keywords: D-Lyxose; D-Mannose; L-Rhamnose; D-Tagatose; D-*manno*-Heptulose; Tungstate complexes; Molybdate complexes; ^{13}C NMR; ^{183}W NMR

1. Introduction

Rare sugars may be synthesized from available natural aldoses by epimerization at C-2 in acidic medium, a reaction that is catalysed by molybdate [1], but not by tungstate,

☆ Dedicated to the memory of Prof. V. Bílik.

* Corresponding author.

SSDI 0008-6215(95)00210-3

ions. The mechanism probably involves transient molybdate complexes in which a C-1/C-2 transposition occurs [2,3]. Many studies have been devoted to the characterization of the relevant molybdate–carbohydrate complexes. The thermodynamic stability constants were determined by potentiometry [4,5] and photometry [6]. The structural identification of the complexes of aldoses and ketoses was attempted by NMR of the ^{1}H, ^{13}C [4,7–11], and ^{95}Mo [4,12] nuclei. Because of the chemical similarity between molybdenum and tungsten, tungstate complexes were often studied as inert models for molybdate species. We have recently developed the use of ^{183}W NMR for the study of tungstate complexes of alditols [13–16]. The interest of this technique lies in the existence of coupling constants between the tungsten atoms and protons of the ligand, which allows the unambiguous assignment of the sites of chelation of each tungsten atom.

The complexes of aldoses and ketoses of the *lyxo* series are known to form molybdate or tungstate complexes stronger than those formed by sugars of any other configuration. The sequence of stabilities is: *lyxo* > *ribo* > *xylo* ≈ *arabino* [6,7], possibly because the major complexes involve the sugars in cyclic form when they are of *lyxo* and *ribo* configuration, and in acyclic form when they are of *arabino* or *xylo* configuration. Nevertheless, small amounts of acyclic complexes are also detected with *lyxo* and *ribo* sugars [9]. The nature of the cyclic form of complexed *lyxo* aldoses was disputed in the literature. Earlier papers described the ligand in the β-pyranose form with either a tridentate [7–10,12] or tetradentate site of chelation [4]. In contrast, a subsequent study showed that the ^{13}C NMR data matched more closely a furanoid conformation than a pyranoid one, and proposed a structure involving the sugars (aldoses or ketoses) in tetradentate β-furanose form [11] for all the complexes of this series. This assumption was in agreement with the X-ray structural determination of a solid D-lyxose-dimolybdate complex [17]. However, data for the D-gulose-dimolybdate complex were reported in a recent paper which concluded that the ligand was in the α-furanose form with the tridentate O-1,2,3 site of chelation [18].

In this work, the reactions of the *lyxo* sugars with disodium tungstate in aqueous solution were examined by multinuclear NMR, with the hope of clarifying the nature of their cyclic complexes. During the course of this study, we discovered that D-mannose and D-*manno*-heptulose formed noticeable amounts of a novel type of complex, in addition to the expected species. Data are presented that demonstrate the participation of one or two chelating oxygen atoms of the side chain in both types of complexes.

2. Experimental

All chemicals were commercial products of analytical grade and were used as received.

The complexes were prepared by mixing the sugar (1 mmol) and disodium tungstate (or molybdate) dihydrate (2 or 2.5 mmol) in deuterium oxide (1 mL) and adding concentrated HCl (1 mmol).

The ^{1}H, ^{13}C, and ^{183}W NMR spectra were obtained at 298 K on Bruker AM 360 and ARX 400 spectrometers equipped with 5- or 10-mm multinuclear probes. Experimental

details have been published elsewhere [13–16]. The stability constants were determined by potentiometry following a published method [4,5].

3. Results

Previous studies have established that the single tungstate complexes of lyxose and rhamnose [11] are structurally related to the major molybdate species [4]. This type of dinuclear complex is ubiquitous with sugars of *lyxo* configuration and is called type L (for *lyxo*) in this paper. There is agreement in the recent literature that the ligands are involved in furanose form, but the denticity of the site of chelation has been reported to be three [18] or four [4,11]. With molybdate, lyxose formed two complexes, one of type L (70%) and a tetradentate chelate (10%) of the acyclic hydrated aldehyde [9], whereas tagatose formed two complexes, the type L (60%) and another furanose species specific of ketoses (20%) [10,11].

When tungstate reacts with tagatose, only six new signals appear in the ^{13}C NMR spectrum, indicating the formation of a single complex of type L, isostructural with the major molybdate complex [11] on the basis of the similarity of their ^{13}C NMR spectra. The ^{183}W NMR spectra of the complexes of lyxose, rhamnose and tagatose (Fig. 1) were recorded and displayed two signals each in the range δ −68 to −93 (Table 1) in agreement with their dinuclear stoichiometry [4,12] and a +VI oxidation state. These signals are generally coupled to vicinal protons of the sugars, which allowed 2D indirect heteronuclear $^{1}H-^{183}W$ correlation experiments, in order to obtain a larger sensitivity [16]. In the three complexes, one tungsten atom is correlated with H-3,5 (aldoses) and H-4,6 (tagatose) and is numbered W-2. The other tungsten atom is correlated with H-1 of lyxose and rhamnose and is numbered W-1. In the tagatose complex, weak correlations were detected between W-1 and H-6′, and W-2 and H-6 respectively, demonstrating that O-6 bridges the tungsten atoms.

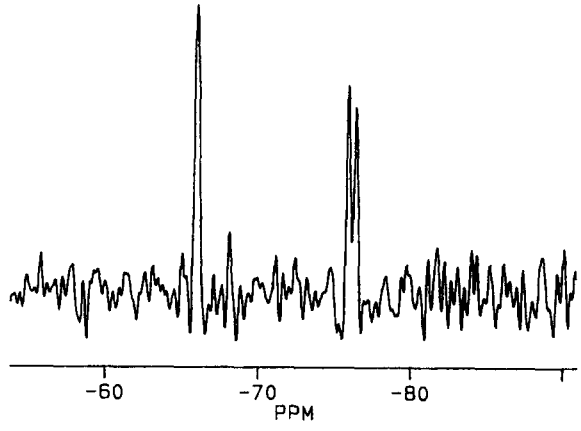

Fig. 1. ^{183}W NMR (15.005 MHz) spectrum of the tungstate complex of D-tagatose (type L) (2500 scans, 2.5 h).

Table 1
^{183}W NMR (15.005 MHz) chemical shifts, δ, and vicinal coupling constants, $^{3}J_{W,H}$, for the tungstate complexes of type L [a]

Tungsten atom	W-1		W-2	
Complex	δ (ppm)	$^{3}J_{W,H}$ (Hz)	δ (ppm)	$^{3}J_{W,H}$ (Hz)
D-Lyxose, type L	−79.6	8.6 (H-1)	−71.1	7.9 (H-3)
		2.4 (H-2)		3.9 (H-5)
D-Mannose, type L	−73.75	6.4 (H-1)	−90.9	7.6 (H-3)
		< 2.5 (H-2)		2.5 (H-5)
				< 2.5 (H-2)
L-Rhamnose, type L	−73.4	5.9 (H-1)	−92.3	7.4 (H-3)
				< 2.5 (H-5)
D-Tagatose, type L	−68.1	< 2.5 (H-3)	−78.4	7.3 (H-4)
		< 2.5 (H-6')		< 2.5 (H-6)
D-*manno*-Heptulose, type L	−70.85	< 2.5 (H-3)	−89.75	7.3 (H-4)
				< 2.5 (H-6)
D-Mannose, type M	15.0	6.3 (H-3)	0.3	9.4 (H-2)
D-*manno*-Heptulose, type M	13.7	< 2.5	−3.6	< 2.5
		< 2.5		

[a] Reference: Na_2WO_4 in alkaline D_2O. Accuracy $\delta \pm 0.1$ ppm, $^{3}J_{W,H} \pm 0.1$ Hz.

The ^{13}C NMR spectra are reported in Tables 2 and 3. When the coordination induced shifts (CIS) are calculated, assuming the uncomplexed ligands to adopt the β-furanose form in which OH-1,2 (HO-2,3 for tagatose) are *cis*, it is found that four carbon atoms are deshielded ($\Delta\delta > 6$ ppm), i.e. C-1,2,3,5 for aldoses and C-2,3,4,6 for tagatose. In contrast, C-4 or C-5, which lack a hydroxyl group, are less affected ($\Delta\delta < \pm 2$ ppm). Thus, there is strong experimental evidence that the ligands are tetradentate in complexes of type L.

When mannose or D-*manno*-heptulose are mixed with two equivalents of tungstate, the ^{13}C NMR spectra indicate the formation of a single complex of type L. The data in Tables 2 and 4 show the analogy with the corresponding molybdate species. The CIS patterns reveal that the sites of chelation are O-1,2,3,5 for mannose and O-2,3,4,6 for D-*manno*-heptulose. Accordingly, the corresponding ^{183}W NMR spectra match closely those for the above complexes (Table 1).

In the case of mannose, a very interesting finding is the observation of three correlation signals for W-2 (δ −90.9) with H-2,3,5. Since in dinuclear species, each tungsten atom is bound to a non-bridging and two bridging oxygen atoms (see Fig. 3), the site of chelation is defined as O-2,3,5 for W-2. Moreover, W-1 (δ −73.75) is strongly correlated with H-1 and weakly correlated with H-2. It is deduced that the bridging atoms are O-2 and O-5 and that the site of chelation for W-1 is O-1,2,5.

A novel series of complexes, named series M (for *manno*), was detected when 2.5 equivalents of tungstate were added to mannose and D-*manno*-heptulose. Both sugars afforded mixtures of the type L (60%) and the type M (40%) species, according to the intensities of the signals in the ^{13}C spectrum. Under the same conditions, mannose did not form a molybdate analogue of type M, in agreement with the literature [9]. On the contrary, D-*manno*-heptulose formed a molybdate complex of type M (45%) in addition

Table 2
^{13}C NMR (90.556 MHz) chemical shifts, δ (in ppm), and direct coupling constants, $^{1}J_{C,H}$ (in Hz), for the tungstate and molybdate complexes of aldoses (type L) and the molybdate complex of D-gulose [a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6
D-Lyxose, β-*f*, δ	96.3	73.2	71.0	82.1	62.7	
W-complex, δ	112.9	84.6	88.3	81.6	68.8	
W-complex, $^{1}J_{C,H}$	174	156	154	154	144	
$\Delta\delta$ (W)	16.6	11.4	17.3	−0.6	6.1	
$\Delta\delta$ (Mo) [b]	*16.5*	*10.9*	*16.7*	*−0.9*	*5.8*	
D-Mannose, β-*f*, δ	96.6	73.1	71.2	80.7	71.0	64.4
W-complex, δ	112.7	84.0	88.0	79.7	79.7	65.2
W-complex, $^{1}J_{C,H}$	180	157	157	153	148	142
$\Delta\delta$ (W)	16.1	10.9	16.8	−1.0	8.7	0.8
$\Delta\delta$ (Mo) [b]	*15.6*	*11.0*	*17.1*	*−1.0*	*8.3*	*0.4*
L-Rhamnose, β-*f*, δ	96.6	73.1	71.4	85.7	67.0	20.0
W-complex, δ	112.5	84.0	88.3	83.3	75.8	23.4
W-complex, $^{1}J_{C,H}$	182	156	156	149	146	125
$\Delta\delta$ (W)	15.9	10.9	16.9	−2.4	8.8	3.4
$\Delta\delta$ (Mo) [b]	*15.7*	*11.4*	*17.6*	*−1.9*	*8.6*	*3.3*
D-Gulose [c]						
Mo-complex, δ [c]	*112.7*	*84.3*	*88.7*	*81.3*	*76.2*	*64.4*
Mo-complex, $^{1}J_{C,H}$ [c]	*177.4*	*156*	*153.4*	*151*	*141.2*	*139.9*

[a] Accuracy $\delta \pm 0.1$ ppm; $^{1}J_{C,H} \pm 1$ Hz. Data for carbon atoms that bear chelating oxygen atoms are underlined. Data for the molybdate complex are in italics.
[b] From ref. [11].
[c] From ref. [18], in which data for the uncomplexed ligand were not reported.

to the type L species (55%). In the literature, the type M complex of D-*manno*-heptulose was attributed to a type of complex common to all ketoses, involving the ligand in pyranose form with a O-1,2,3 site [10].

Table 3
^{13}C NMR (90.556 MHz) chemical shifts, δ (in ppm) and direct coupling constants $^{1}J_{C,H}$ (in Hz), for the tungstate and molybdate complexes of D-tagatose (type L) [a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6
u, β-*f*, δ [b]	63.5	103.3	71.7	71.8	80.9	61.9
Mo-complex, δ [b]	*65.2*	*119.9*	*84.9*	*87.6*	*82.4*	*68.2*
$\Delta\delta$ [b]	*1.7*	*16.6*	*13.2*	*15.8*	*1.5*	*6.3*
W-complex, δ	66.4	120.9	85.2	88.0	81.0	68.8
$^{1}J_{C,H}$	145	—	159	156	153	142
$\Delta\delta$	0.9	17.6	13.5	16.2	0.1	6.9

[a] u, Uncomplexed. Accuracy $\delta \pm 0.1$ ppm; $^{1}J_{C,H} \pm 1$ Hz. Data for carbon atoms that bear chelating oxygen atoms are underlined. Data for the molybdate complex are in italics.
[b] From ref. [11].

Table 4
^{13}C NMR (90.556 MHz) chemical shifts, δ (in ppm) and direct coupling constants $^{1}J_{C,H}$ (in Hz), for the tungstate and molybdate complexes of D-*manno*-heptulose (type L) [a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7
u, β-*f*, δ [b]	63.5	103.3	71.7	71.8	80.9	71.0	64.4
Mo-complex, δ	*65.6*	*120.3*	*85.5*	*88.7*	*81.9*	*81.5*	*65.4*
$^{1}J_{C,H}$	*144*	—	*157*	*157*	*151*	*146*	*145*
$\Delta\delta$	*2.1*	*17.0*	*13.8*	*16.9*	*1.0*	*10.5*	*1.0*
W-complex, δ	65.9	120.5	84.8	88.0	81.0	79.7	65.7
$^{1}J_{C,H}$	144	—	155	156	150	146	144
$\Delta\delta$	2.4	17.2	13.1	16.2	0.1	8.7	1.3

[a] u, Uncomplexed. Accuracy $\delta \pm 0.1$ ppm; $^{1}J_{C,H} \pm 1$ Hz. Data for carbon atoms that bear chelating oxygen atoms are underlined. Data for the molybdate complex are in italics.
[b] These values cannot be directly measured because of the very low proportion of *f* forms at equilibrium and are estimated from the chemical shifts for D-tagatose and D-mannose in β-*f* form. The proposed values are reasonably close to the partial assignments of Angyal and Tran [20].

The ^{13}C spectra of the complexes of type M (Table 5) were assigned from 2D heteronuclear $^{1}H-^{13}C$ correlation experiments. The primary carbon of the side chain is obviously deshielded and thus belongs to the site of chelation. Furthermore, when the CIS patterns are calculated, reasonable values are obtained only when the uncomplexed ligands are in α-furanose form, showing that the deshielded carbon atoms are C-2,3,5,6 for mannose and C-3,4,6,7 for D-*manno*-heptulose. If the pyranose forms are considered, it appears that all carbon atoms would be considerably deshielded, including those that do not bear hydroxyl groups.

Table 5
^{13}C NMR (90.556 MHz) chemical shifts, δ (in ppm) and direct coupling constants $^{1}J_{C,H}$ (in Hz), for the complexes of D-mannose (type M) and D-*manno*-heptulose (type M) [a]

D-Mannose	C-1	C-2	C-3	C-4	C-5	C-6	
u, α-*f*, δ	102.7	77.9	72.5	80.5	70.6	64.5	
W-complex, δ	103.6	89.7	79.5	77.5	82.6	74.3	
$^{1}J_{C,H}$	174	157	146	152	148	145	
$\Delta\delta$	0.9	11.8	7.0	−3.0	12.0	9.8	
D-*manno*-Heptulose	C-1	C-2	C-3	C-4	C-5	C-6	C-7
u, α-*f*, δ [b]	64.0	105.7	77.6	71.9	80.0	70.6	64.5
Mo-complex, δ	*64.7*	*111.1*	*88.7*	*81.5*	*79.7*	*82.9*	*73.8*
$^{1}J_{C,H}$	*145*	—	*154*	*145*	*158*	*145*	*147*
$\Delta\delta$	*0.7*	*5.4*	*11.1*	*9.6*	*−0.3*	*12.3*	*9.3*
W-complex, δ	64.5	110.5	88.5	79.7	78.8	82.2	74.3
$^{1}J_{C,H}$	142	—	154	145	158	145	147
$\Delta\delta$	0.5	4.8	10.9	7.8	−1.2	11.6	9.8

[a] u, Uncomplexed. Accuracy $\delta \pm 0.1$ ppm; $^{1}J_{C,H} \pm 1$ Hz. Data for carbon atoms that bear chelating oxygen atoms are underlined. Data for the molybdate complex are in italics.
[b] These values cannot be directly measured because of the very low proportion of *f* forms at equilibrium and are estimated from the chemical shifts for D-tagatose and D-mannose in the α-*f* form.

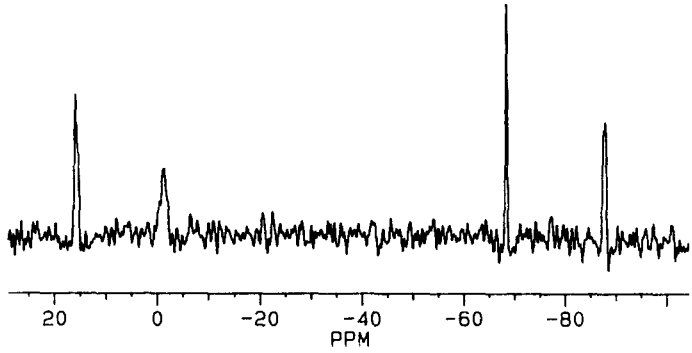

Fig. 2. ^{183}W NMR (15.005 MHz) spectrum of the mixture of tungstate complexes of D-*manno*-heptulose (1500 scans, 1.5 h). The signals at δ −70 and −89 correspond to the complex of type L, whereas those at δ 13 and −3 belong to the complex of type M.

In order to confirm that a carbon atom bears a chelating oxygen atom, the values of the direct coupling constants $^{1}J_{C,H}$ are often examined, since they are generally enhanced by 2–10 Hz in such a case. Unfortunately, the coupling constants for the free ligands could not be measured because the proportions of furanose forms are negligible at equilibrium, but they were assumed to be close to 142 Hz for all carbons, as in the pyranose forms. In consequence, the values > 150 Hz found for C-4 (mannose) and C-5 (D-*manno*-heptulose) are surprisingly large for atoms that do not belong to the sites of chelation, although the small negative values of CIS clearly demonstrate that they do not bear chelating oxygen atoms (Table 5).

The ^{183}W NMR spectra of the complexes of type M (Fig. 2) differ from those of type L (Fig. 1). These complexes are also dinuclear species, since two signals are found near δ 15 (W-1) and δ −2 (W-2). For the D-mannose complex, vicinal coupling constants with a single proton were measured for both signals, but not for D-*manno*-heptulose (Table 1). Correlation experiments indicated that W-1 was correlated with H-3 and W-2 with H-2. The sites of chelation for each tungsten atom were defined by examination of molecular models. As in all other dinuclear tungstate complexes of tetradentate carbohydrates, each tungsten atom is chelated by three oxygen atoms, two of them acting as bridges. W-1 is bound to O-3,5,6 and W-2 to O-2,3,5 of mannose (O-4,6,7 and O-3,4,6, respectively, for D-*manno*-heptulose). The likely structure is represented in Fig. 3, in which the inorganic moiety is composed of two WO_6 octahedra sharing a face that includes O-3,5 of mannose and a bridging oxygen atom O_b. Note that C-2;O-2;W-2;O_b;W-1;O-6;C-6 are aligned. The dihedral angles W-2–O-2–C-2–H-2 and W-1–O-3–C-3–H-3 are consistent with the observed vicinal coupling constants.

The complexation of D-gulose was not investigated in this work, but a comparison can be made with its molybdate complexes which were recently studied [18]. The major species (90%) is obviously of type L, as its ^{13}C spectrum is very close to those of all complexes of this series (Table 2). The minor species (5%) is an acyclic complex. No complex of type M was observed, in agreement with the absence of this species in the

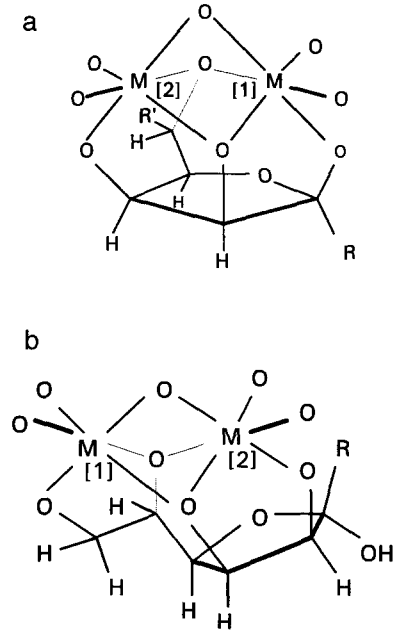

Fig. 3. Proposed structures for the molybdate and tungstate complexes (M = Mo or W). (a) type L: D-lyxose, R = R′ = H; D-mannose and L-gulose, R = H, R′ = CH_2OH; D-rhamnose, R = H, R′ = CH_3; D-tagatose, R = CH_2OH, R′ = H; D-*manno*-heptulose, R = R′ = CH_2OH. (b) type M: D-mannose, R = H; D-*manno*-heptulose, R = CH_2OH. Actually, L-rhamnose was used in the work, but the structures are more easily compared with the D-isomer.

mannose–molybdate system. The authors claimed that in the complex of type L, the ligand was in furanose form with a O-1,2,3 site of chelation, because they considered that the unchanged direct coupling constant for C-5 (141.2 Hz) ruled out the participation of O-5 in the site of chelation. However, the present data show that in several tungstate and molybdate complexes of type L, the carbon atom of the side chain that bears a donating oxygen atom also possesses a direct coupling constant close to its value in the uncomplexed sugar [lyxose, C-5, 144 (W) 145 (Mo); mannose, C-5, 148 (W) 145 (Mo); rhamnose, C-5, 146 (W and Mo); tagatose, C-6, 142 (W); D-*manno*-heptulose, C-6, 146 (W and Mo)]. This finding indicates that, if used alone, the magnitude of the direct coupling constant is not a safe criterion for assignment of a carbon atom to the site of chelation. On the contrary, the observation of a correlation in the 2D ^{1}H–^{183}W spectrum between a tungsten atom and a proton of the ligand demonstrates the existence of a W–O–C–H path between them and hence the presence of a chelating oxygen atom. It must be concluded that, like all other sugars that afford complexes of type L, gulose is a tetradentate ligand (O-1,2,3,5) in its molybdate complex. This would probably be the case for its tungstate complex also.

In order to compare the overall stabilities of the complexes, the formation constants of the tungstate and molybdate complexes of tagatose and mannoheptulose were

Table 6
Formation constants (log K_{212}) of the molybdate and tungstate complexes [a]

Sugar	D-Lyxose[b]	D-Mannose[b]	L-Rhamnose[b]	D-Tagatose	D-*manno*-Heptulose
M = Mo	15.00	14.50	13.90	16.35	16.25
M = W	18.10	17.50	17.05	19.10	18.75

[a] By potentiometry (t, 25°C, KCl 0.1 M). K_{212} is the equilibrium constant for the reaction: $2\ MO_4^{2-} + H_nL + 2\ H^+ \rightleftarrows [(MO_2)_2O(H_{n-4}L)]^{2-} + 3\ H_2O$.
[b] From ref. [4].

determined by the usual potentiometric method [4,5]. The equilibrium is written (M represents either Mo or W):

$$2\ MO_4^{2-} + H_nL + 2\ H^+ \rightleftarrows \left[(MO_2)_2O(H_{n-4}L)\right]^{2-} + 3\ H_2O$$

The corresponding values (log K_{212}) are compared to those previously found for the aldoses in Table 6 [4,5]. As for all complexes of sugars and alditols, the formation constants of tungstate species are ca. three units higher than those for molybdate [13]. The complexes of ketoses are definitely stronger than those of aldoses, since the values are ca. one unit higher than for lyxose. Thus, the presence of a hydroxymethyl group at C-2 enhances the stability of the complex. A possible explanation may be that uncomplexed ketoses have a higher proportion of furanose forms at equilibrium than aldoses.

4. Discussion

Our results clearly demonstrate that aldoses and ketoses of the *lyxo* series form two series of molybdate or tungstate complexes in which the sugars are tetradentate and adopt the furanose form. Type L is obtained when three hydroxyl groups of the ring are *cis*, while type M is formed when the anomeric hydroxyl group is *trans* to the other groups borne by the ring. One side chain oxygen atom in type L and two in type M are involved in the site of chelation, in agreement with the finding that only mannose and D-*manno*-heptulose afford species of type M. Since mannose and gulose do not form molybdate species of type M, in contrast to D-*manno*-heptulose, type M seems to be formed more readily with tungstate than with molybdate. Besides, like mannose, gulose would be expected to form a tungstate complex of type M.

The structure of complexes of type L, deduced from NMR data (Fig. 3), is fully consistent with that obtained by X-ray crystallography for a solid lyxose–dimolybdate complex [17], in which O-5 was clearly shown to bridge the molybdenum atoms. Interesting comments were made on the structure of the furanose ring, described as an intermediate between ${}^4E$ and ${}^4_oT$, where C-4 was 'pushed out' of the plane of the ring in order to bring O-5 closer to the dimolybdate group. As discussed below, this may be the reason for the anomalous coupling constant found for C-4 of aldoses and C-5 of ketoses in complexes of series L.

NMR data.—Because few data on the chemical shifts of tungsten atoms in their carbohydrate complexes are available, some comments are necessary. First, values for complexes of type L are comparable to those found for complexes of tetradentate alditols in which all four hydroxyl groups are vicinal, typically around δ −75 in *sickle* conformation [13] and δ −90 in *zigzag* conformation [16]. On the other hand, values for complexes of type M lie in a more characteristic range, close to δ 0. Secondly, the effects of the substituents borne by the ring may be examined for series L from data in Table 1. By comparing lyxose and tagatose, it can be seen that the presence of a hydroxymethyl group at C-2 has opposite effects on W-1, which is deshielded by 10 ppm, and on W-2, which is shielded by 8 ppm. By comparing lyxose with mannose and rhamnose, it was found that the presence of the side chain at C-4 deshields W-1 (6 ppm) and shields W-2 (20 ppm). In the case of D-*manno*-heptulose, which bears substituents at C-2 and C-5, the effect of the C-5 substituent prevails for W-2 (shielding 20 ppm), whereas that of the C-2 substituent prevails for W-1 (deshielding 10 ppm). These results agree with the proposed structure, since W-1 is closer to C-2 in ketoses and W-2 is closer to C-4 in aldoses and C-5 in ketoses. The small number of compounds of type M does not permit a similar discussion.

The direct coupling constants exhibit surprising values in both series. The one for C-4 (C-5), which is not part of the site of chelation, is larger than expected. A possible reason is that C-4 is located slightly out of the ring plane, as reported in the solid-state structure. It may allow an enhanced overlap of the orbitals of the CH-4 bond with the lone pairs of the ring oxygen atom, which increases the corresponding direct coupling constant. Inversely, for the side chain atoms C-5 (C-6) in series L and M, and C-6 (C-7) in series M, that bear donating oxygen atoms, the surprisingly low coupling constants may be due to a reduced overlap. Such discrepancies may cause erroneous identification of the site of chelation [18] when the CIS effects are overlooked. One may also remark that, in complexes of series M (Table 5), the magnitude of the direct coupling constant of the ring atom C-3 (C-4 for the ketose) is little enhanced ($\Delta J < 5$ Hz) when compared to the neighbouring C-2 (C-3) ($\Delta J > 10$ Hz).

Comparison of the stabilities of the complexes.—For tungstate complexes, species of type L are slightly stronger than those of type M, according to their relative proportions at equilibrium. Accordingly, the sugars with the longest side chain at C-4 (mannose and D-*manno*-heptulose) form the weaker complexes, because they form species of type M besides those of type L. For molybdate species, the situation is not so simple, because other types of complexes occur. For example, with tagatose, the major species was of type L and the minor species was a tridentate complex (ligand α-furanose, site O-1,3,4, type K) [11]. However, no molybdate complex of type K was observed for D-*manno*-heptulose, which instead afforded the complex of type M. Finally, the aldoses also form molybdate acyclic complexes [9] in low yield (< 10%). This defines the sequence of stabilities as: type L > type M > type K > acyclic species. Tungstate complexes of type K were not observed in this work.

The tendency of molybdate and tungstate to complex sugars in furanose form rather than in pyranose form does not appear to be a rare phenomenon, since it is also the case for ketoses of the *lyxo* and *ribo* series (tagatose and psicose, respectively) which form molybdate complexes of type K in which the ligands are tridentate (O-1,3,4 sites) [11].

Another example of this tendency is given by the report that molybdate reacts with 3-hydroxy-2-butanone (acetoin) to yield a complex characterized by X-ray crystallography [19] in which the dimolybdate core is chelated by a 2,3,4,5-tetrahydroxy-2,3,4,5-tetramethylfuranose ring. It seems that molybdate acts as a template in promoting the aldol condensation of the reactant that affords the final tetradentate ligand. Interestingly, the spontaneous dimerization of acetoin in the absence of molybdate only gives a pyranoid bis-hemiacetal, showing that molybdate is indeed responsible for the cyclization to a furanose product.

5. Conclusions

Each anomer of the *lyxo* furanose sugars forms a distinct series of tungstate and molybdate complexes in which the ligands are tetradentate. In the more stable complexes (series L), the site of chelation includes three *cis* vicinal ring oxygen atoms and O-5 (aldoses) or O-6 (ketoses), in agreement with crystallographic data reported for the solid lyxose–dimolybdate complex. Support for a similar structure in solution is provided by the existence of coupling constants between a tungsten atom and H-5 or H-6. The weaker complexes (series M) require sugars that possess two vicinal hydroxyl groups on the side chain borne at C-4 (aldoses) or C-5 (ketoses). The ligand is the anomer in which the anomeric hydroxyl group is *trans* to HO-2,3 (aldoses) or HO-3,4 (ketoses). The site of chelation is O-2,3,5,6 (aldoses) or O-3,4,6,7 (ketoses) and the corresponding carbon atoms, which display large coordination-induced shifts, are unambiguously identified by 2D NMR. Thus, strong experimental evidence indicates the presence of chelating oxygen atoms in the side chain of the sugars.

Acknowledgement

The authors thank Dr J. P. Sauvage for measurements of the formation constants of the complexes.

References

[1] V. Bílik, *Chem. Zvesti*, 26 (1972) 76–81; 183–186; 187–189; 372–375.
[2] M.L. Hayes, N.J. Pennings, A.S. Serianni, and R. Barker, *J. Am. Chem. Soc.*, 104 (1982) 6764–6769.
[3] E.L. Clark, Jr., M.L. Hayes, and R. Barker, *Carbohydr. Res.*, 153 (1986) 263–270.
[4] J.F. Verchère and S. Chapelle, *Polyhedron*, 8 (1989) 333–340.
[5] J.F. Verchère, J.P. Sauvage, and G.R. Rapaumbya, *Analyst*, 115 (1990) 637–640.
[6] J.P. Sauvage, S. Chapelle, A.M. Dona, and J.F. Verchère, *Carbohydr. Res.*, 243 (1993) 293–305.
[7] J. Alföldi, L. Petruš, and V. Bílik, *Collect. Czech. Chem. Commun.*, 43 (1978) 1476–1480.
[8] J. Alföldi, V. Bílik, and L. Petruš, *Collect. Czech. Chem. Commun.*, 45 (1980) 123–126.
[9] V. Bílik and M. Matulová, *Chem. Pap.*, 44 (1990) 257–265.
[10] M. Matulová and V. Bílik, *Chem. Pap.*, 44 (1990) 97–103.
[11] J.P. Sauvage, S. Chapelle, and J.F. Verchère, *Carbohydr. Res.*, 237 (1992) 23–32.
[12] M. Matulová and V. Bílik, *Chem. Pap.*, 44 (1990) 703–709.

[13] S. Chapelle and J.F. Verchère, *Inorg. Chem.*, 31 (1992) 648–652.
[14] S. Chapelle, J.P. Sauvage, and J.F. Verchère, *Inorg. Chem.*, 33 (1994) 1966–1971.
[15] S. Chapelle and J.F. Verchère, *Carbohydr. Res.*, 266 (1995) 161–170.
[16] S. Chapelle, J.P. Sauvage, P. Köll, and J.F. Verchère, *Inorg. Chem.*, 34 (1995) 918–923.
[17] G.E. Taylor and J.M. Waters, *Tetrahedron Lett.*, 22 (1981) 1277–1278.
[18] M. Matulová and V. Bílik, *Carbohydr. Res.*, 250 (1993) 203–209.
[19] S. Liu and J. Zubieta, *Polyhedron*, 8 (1989) 1213–1215.
[20] S.J. Angyal and T.Q. Tran, *Aust. J. Chem.*, 36 (1983) 937–946.