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A ^{13}C and ^{183}W NMR study of the structures of tungstate and molybdate complexes of volemitol

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Abstract

^{1}H, ^{13}C, and ^{183}W NMR spectroscopic methods were used for the structural characterization of the tungstate and molybdate complexes of volemitol (D-*glycero*-D-*manno*-heptitol) in aqueous solution. The major species (type E) are a pair of isomeric complexes formed at the *arabino* site in reversed orientation, i.e., HO-1,2,3,4 and HO-4,3,2,1. A single, minor complex is formed at the HO-3,4,5,6 *altro* site and is shown to be isostructural with the known single complexes of ribitol and D-altritol (type E'). The present NMR results support the hypothesis that complexes of type E' are weaker than those of type E because they are destabilized by a steric strain due to the interaction of the side chain of the ligand with the site of chelation.

Keywords: Volemitol; D-*glycero*-D-*manno*-Heptitol; Tungstate complexes; Molybdate complexes; ^{13}C NMR; ^{183}W NMR

1. Introduction

The formation of molybdate and tungstate chelates is a useful reaction that allows the separation of neutral carbohydrates as charged species by electrophoresis [1–6] and chromatography [7]. Most of these complexes are dinuclear [8–10] and their structures and stabilities are known to strongly depend on the configuration of the site of chelation of the carbohydrate ligand. In the case of alditols $HOCH_2$–$(CHOH)_{n-2}$–CH_2OH, previous studies of the molybdate [11–13] and tungstate [13–16] complexes have generally been limited to compounds with $n \leq 6$, with the exception of some heptitols ($n = 7$) including perseitol [17–19] (D-*glycero*-D-*galacto*-heptitol) and volemitol (D-*glycero*-D-*manno*-heptitol)

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[18,19]. These heptitols are natural compounds involved in the metabolism of plants [20].

^{1}H and ^{13}C NMR spectroscopy have been widely used for the structural characterization of carbohydrate ligands in their molybdate and tungstate complexes. Attempts to study the inorganic moieties by ^{95}Mo NMR gave poor results [11,19], because the broad signals are not helpful in the characterization of the environment of the molybdenum atoms. In contrast, we have recently reported the use of ^{183}W NMR spectroscopy [16] for the characterization of tungstate complexes of carbohydrates. The spectra always display sharp signals that ensure a fast determination of the number and types of all the complexes present, even in complicated mixtures. Moreover, the coupling of the tungsten atoms to some protons of the ligand allows the assignment of the site of chelation of the carbohydrate.

Previous studies have established [11] that the complexes in which the site of chelation has the *erythro* configuration (type E) are generally favoured with respect to those involving a *threo* site (type T). Moreover, the complexes of type E formed with molybdate and tungstate have similar structures in which the tetradentate ligands are in a sickle conformation, but the complexes of type T are different: the ligands are tetradentate in molybdate compounds and tridentate in tungstate species [16].

Complexes of type E have been clearly characterized for ligands possessing *erythro*, *ribo*, *arabino*, and *galacto* sites of chelation. The case of *altro* sites is not so clear. The formation of a single complex of D-altritol involving the *altro* HO-2,3,4,5 site has been reported [18,19]. Another alditol of interest is volemitol or α-sedoheptitol, a natural polyol that occurs in the mushroom *Lactarius volemus* [21]. This heptitol may form complexes at several possible sites of chelation involving secondary hydroxyl groups in *arabino*, *altro*, *manno*, and *ribo* configurations.

The molybdate complexes of volemitol have been studied by ^{1}H and ^{13}C NMR spectroscopy [18,19]. Three complexes were detected, but the third one could not be structurally defined from the NMR data. One of the complexes was assigned as involving the HO-4,5,6,7 system, whereas the second one showed chelation at the HO-3,4,5,6 site. A subsequent study by ^{95}Mo NMR confirmed both complexes to belong to type E. These results agree with the rule that complexes formed at the *manno* site HO-2,3,4,5 would be of very low stability, as in the cases of the complexes of mannitol [8,9,11,17] and perseitol [17].

The tungstate complexes of volemitol have not been described in the literature. This study was undertaken in order to use ^{183}W NMR for their characterization and for a comparison of the affinities of the different possible sites of chelation for molybdate and tungstate.

2. Experimental

Volemitol was prepared in the Laboratory of the Slovak Academy of Sciences, Bratislava, and was kindly donated by Dr. Maria Matulová. All other chemicals were commercially available products of the purest grade and were used as received. The sources of inorganic ions were disodium molybdate or tungstate dihydrates. All samples were prepared in D_2O, with a slight excess of the inorganic anion with respect to the alditol L. The ratio MO_4^{2-}:L was 2.5 (M = Mo or W). The concentration of alditol was 1.0 M for ^{183}W NMR spectroscopy and 0.2 M for ^{1}H and ^{13}C NMR spectroscopy.

The pH of the solutions of complexes was adjusted by the dropwise addition of a concentrated solution of HCl (ca. 12 M) and was measured using a Metrohm pH-meter equipped with a Radiometer MI-412 micro-combination glass electrode (external diameter 2 mm).

Experimental details for the recording of ^{13}C NMR spectra have been described in preceding papers [11,16]. The experiments were performed at 298 K using either a Bruker AM 360 multinuclear spectrometer equipped with 5-mm dual (^{1}H–^{13}C) and 10-mm VSP probes, or a Bruker AMX 400 multinuclear spectrometer equipped with a 5-mm VSP probe, in the indirect mode.

1D ^{183}W NMR studies were performed on the AM 360 spectrometer at 15.005 MHz with a pulse width of 30 μs corresponding to a 60° tip angle, a sweep range of 8000 Hz, an acquisition time of 2 s, a relaxation delay of 3 s, and a digital resolution of 3 Hz/pt. 2D NMR ^{13}C–^{1}H heteronuclear correlation shift experiments were made using polarization transfer from ^{1}H to ^{13}C through $^{1}J_{C,H}$ coupling constants [22].

The AMX 400 spectrometer was used for 2D ^{1}H–^{183}W correlation shift experiments made via heteronuclear zero and double quantum coherence using the indirect mode [23]. The durations of the 90° tip angles were 9 μs for ^{1}H and 39 μs for ^{183}W. Optimization was obtained for long-range $^{3}J_{W,H}$ coupling constants with values of 8–10 Hz.

3. Results

^{13}C NMR of tungstate complexes.—The spectrum of uncomplexed volemitol was assigned (Table 1) in agreement with literature data [18]. The addition of a slight excess (ratio WO_4^{2-}/L:2.5) of disodium tungstate at pH 7.5 caused the disappearance of the signals of the free ligand, while 21 new signals appeared that were attributed to the formation of 3

Table 1
90.556-MHz ^{13}C NMR chemical shifts δ and $^{1}J_{C,H}$ direct coupling constants of volemitol and its tungstate complexes

Parameter	Carbon position 1	2	3	4	5	6	7
u, δ (ppm) [a]	64.3	71.7	70.45	70.55	72.4	73.8	63.05
V_1, δ (ppm)	71.8	81.9	90.7	78.45	71.7	75.1	63.1
$^{1}J_{C,H}$ (Hz)	149.2	150.6	150.6	144.6	143.4	141.5	142.9
$\Delta\delta$ (ppm)	7.5	10.2	20.25	7.9	−0.7	1.3	0.05
V_2, δ (ppm)	69.9	91.5	82.0	80.7	72.4	74.1	62.7
$^{1}J_{C,H}$ (Hz)	144.8	152.0	148.4	146.5	143.9	142.2	142.7
$\Delta\delta$ (ppm)	5.6	19.8	11.55	10.15	0.0	0.3	−0.35
V_3, δ (ppm)	63.7	72.6	78.6	89.0	82.0	85.6	63.1
$^{1}J_{C,H}$ (Hz)	143.4	144.8	145.3	148.5	152.0	148.5	140.9
$\Delta\delta$ (ppm)	−0.6	0.9	8.15	18.45	9.6	11.8	0.05

[a] $^{1}J_{C,H}$ = 141 Hz for all carbons. δ assigned from the literature [18]. u, Uncomplexed. Accuracy: $\delta \pm 0.1$ ppm; $^{1}J_{C,H} \pm 0.1$ Hz. Carbons that bear the chelating oxygen atoms are underlined.

Table 2
90.556-MHz ^{13}C NMR chemical shifts δ and $^{1}J_{C,H}$ direct coupling constants of volemitol and of its molybdate complexes

Parameter	Carbon position 1	2	3	4	5	6	7
u, δ (ppm) [a]	64.3	71.7	70.45	70.55	72.4	73.8	63.05
V'_1, δ (ppm)	73.1	82.85	91.2	79.3	71.5	75.9	63.4
$^{1}J_{C,H}$ (Hz)	146.3	149.1	148.5	144.1	141.9	141.3	142.1
$\Delta\delta$ (ppm)	8.8	11.15	20.75	8.75	−0.9	2.1	0.35
V'2, δ (ppm) [b]	70.4	91.8	83.0	82.0	72.6	74.2	62.75
$^{1}J_{C,H}$ (Hz)	145.8	146.8	148.4	146.3	144.9	142.1	143.0
$\Delta\delta$ (ppm)	6.1	20.1	12.55	11.45	0.2	0.4	−0.3
V'_3, δ (ppm)	64.6	72.9	79.7	89.3	82.75	86.6	62.9
$^{1}J_{C,H}$ (Hz)	141.2	144.4	141.8	152.1	149.1	148.3	141.2
$\Delta\delta$ (ppm)	0.3	1.2	9.25	18.75	10.35	12.8	−0.15

[a] $^{1}J_{C,H}$ = 141 Hz for all carbons. δ Assigned from the literature [18]. [b] In agreement with complex *A* [18] (complex V'_1 was not reported). [c] In agreement with complex *C* [18], except reversed assignments for C-1,7. u, Uncomplexed. Accuracy: $\delta \pm 0.1$ ppm; $^{1}J_{C,H} \pm 0.1$ Hz. Carbons that bear the chelating oxygen atoms are underlined.

complexes, represented in the order of decreasing proportions by V_1, V_2 (38% each), and V_3 (24%). The identification of the peaks corresponding to species V_1 and V_2 was made easier by the observation that the proportion of V_1 was slightly enhanced at pH 9.2 (hence the choice of this species as the major V_1 species). Unfortunately, at pH > 9, the spectrum was complicated by the presence of uncomplexed ligand. Finally, the complete assignment of the signals (in the spectrum obtained at pH 7.5) was achieved after a preliminary assignment of the ^{1}H NMR spectrum through a 2D homonuclear ^{1}H–^{1}H correlation experiment [24], followed by a 2D heteronuclear ^{13}C–^{1}H correlation experiment via the $^{1}J_{C,H}$ coupling constants.

In the spectra of the complexes, the signals of the carbon atoms that bear the coordinating oxygen atoms are specifically deshielded. This effect of the chelated metal group on the chemical shifts of the ligand is well documented and is referred to as the coordination induced shift (CIS) [25]. We have previously demonstrated that, because the ligand is forced into a rigid conformation in the complex, carbohydrates possessing sites of chelation of a given configuration form homologous series of complexes [11]. Accordingly, the CIS patterns of such series of complexes are highly characteristic of the geometry of the site of chelation. Complex formation also increases the $^{1}J_{C,H}$ coupling constants of the carbons that belong to the site of chelation.

Table 1 presents the chemical shifts and the $^{1}J_{C,H}$ coupling constants for the carbon atoms of free and complexed volemitol. Because only C-5,6,7 are not deshielded in the major complexes V_1 and V_2, these complexes possess the same site of chelation HO-1,2,3,4, with reversed CIS patterns (7-10-20-8 vs. 6-20-12-10). This behaviour characterizes the pairs of isomeric complexes formed at *arabino* sites [11]. The third minor complex V_3 is shown to involve the *altro* HO-3,4,5,6 site with a slightly different CIS pattern (8-18-10-12) that is nevertheless close to that for type E complexes.

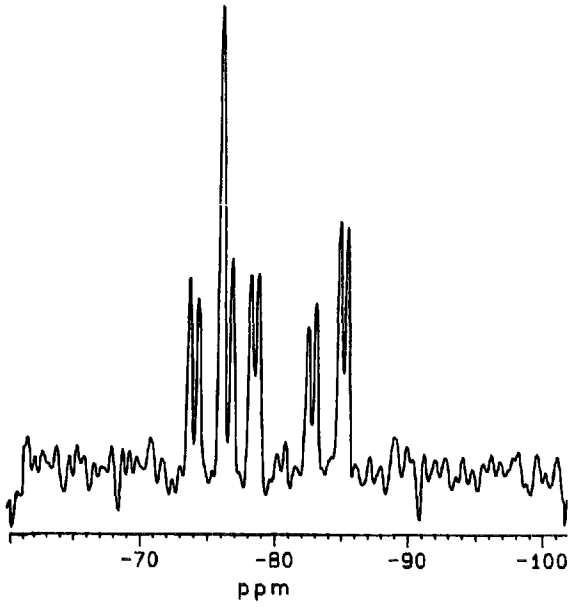


Fig. 1. 15.005-MHz ^{183}W NMR spectrum of the mixture of tungstate complexes of volemitol (3500 scans, 3.5 h).

^{13}C NMR of molybdate complexes.—Since molybdate and tungstate complexes of alditols are known to be isostructural when they belong to type E [25], we compared the present results for the tungstate complexes of volemitol with those reported in the literature for the molybdate species [18,19]. Two complexes only had been identified that match closely the tungstate species V_2 and V_3. A ^{95}Mo NMR study [19] had revealed that both complexes were of type E, with the ligand being in a sickle conformation. A third species had also been detected [18] but could not be identified. We found it surprising that no species corresponding to the major tungstate species V_1 had been reported. Thus, a reinvestigation of the molybdate complexes of volemitol appeared desirable.

The study was made under the same conditions as for the tungstate complexes. The ^{13}C NMR spectrum of an acidified solution of disodium molybdate containing molybdate in slight excess (2.5 equiv) displays 21 new signals indicating the presence of three complexes V'_1 (46%), V'_2 (33%), and V'_3 (21%). After the assignment of the signals of each complex, we noticed a striking similarity between the molybdate and tungstate species (Tables 1 and 2). It is therefore demonstrated that volemitol affords the same complexes, in similar proportions, by reaction with either tungstate or molybdate.

^{183}W NMR.—The spectrum of a tungstate–volemitol mixture shows five multiplets (Fig. 1) in the range between -70 and -90 ppm, characteristic for the formation of dinuclear complexes of type E [25]. Four signals are clearly doublets in which a coupling constant could be measured. The last signal (δ -76.6 ppm) was more intense and could be assigned using a gaussian multiplication of the free induction decay which enhanced the resolution. After deconvolution, this signal was attributed to a singlet and an overlapping doublet. It may be concluded that six magnetically nonequivalent tungsten atoms are present, in agreement with the finding of three complexes by ^{13}C NMR. The signals were assigned (Table 3), first owing to their different intensities, and then the observation of $^3J_{W,H}$ coupling constants allowed the correlation of each tungsten atom to one or several proton(s) of volemitol. 2D NMR indirect ^1H–^{183}W heteronuclear correlation experiments, via long-distance coupling, were used for this purpose [22].

Table 3
15.005-MHz ^{183}W NMR chemical shifts δ and $^{1}J_{C,H}$ coupling constants of tungstate complexes of volemitol and ribitol [a]

Species	Parameter	W-1	W-2	$\Delta\delta$ (ppm)
V_1	δ (ppm)	−76.9	−85.8	8.9
	$^{3}J_{W,H}$ (Hz)	10.0 (H-3)	8.2 (H-1)	
V_2	δ (ppm)	−74.6	−79.1	4.5
	$^{3}J_{W,H}$ (Hz)	9.1 (H-2)	8.8 (H-4)	
V_3	δ (ppm)	−76.6	−83.4	6.8
	$^{3}J_{W,H}$ (Hz)	unresolved	9.5 (H-4)	
Ribitol complex [b]	δ (ppm)	−72.1	−83.9	11.8
	$^{3}J_{W,H}$ (Hz)	unresolved	10.3 (H-2)	

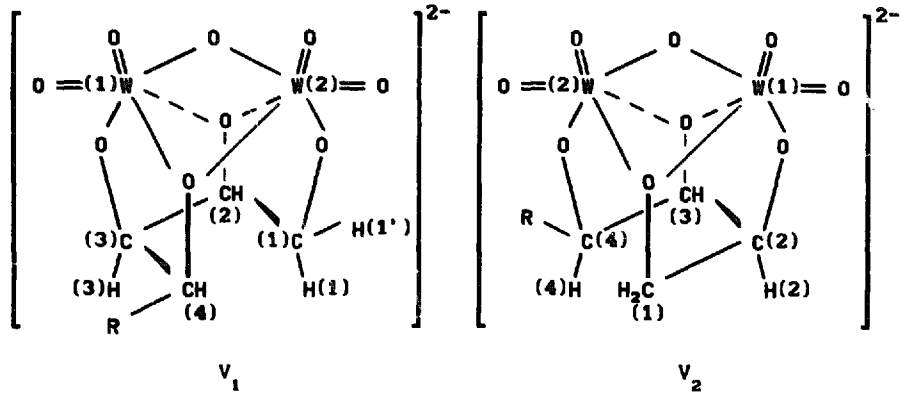
[a] Reference: Na_2WO_4 in alkaline D_2O (by the substitution method [26]). [b] From Ref. [25]. Accuracy: $\delta \pm 0.1$ ppm, $^{3}J_{W,H} \pm 0.1$ Hz.

In V_1, the W-1 atom was strongly coupled to H-3 and weakly correlated with H-4, whereas W-2 was strongly coupled to H-1 (but not with H-1'). These results were compared with those for other complexes of type E (Table 4) in which the ligands always adopt a

Table 4
^{13}C NMR coordination induced shift deshielding patterns ($\Delta\delta$ in ppm) for the four carbons that bear the coordinating oxygen atoms in molybdate and tungstate complexes of alditols with *erythro* sites of chelation

Alditol	Mo complexes [a]					W complexes [b]			
Series E, tetradentate ligands of *erythro* or *arabino* configuration									
Erythritol	E	**6.6**	18.5	9.2	**9.6**	**6.1**	18.1	8.1	**8.4**
D-Glucitol	G_1	**6.3**	19.7	10.5	12.1	**6.0**	19.5	9.8	11.5
	G_2	7.2	19.0	11.5	**9.1**	8.5	18.8	11.8	**8.1**
D-Arabinitol	A_1	**6.6**	19.8	11.4	11.7	**5.9**	19.2	10.4	10.4
	A_2	7.5	19.8	10.6	**9.0**	7.0	19.2	10.2	**7.9**
D-Mannitol	M_1	**5.9**	18.9	12.2	11.7	**5.2**	18.3	11.1	10.3
	M_2	8.7	20.7	9.6	**8.3**	7.5	20.0	8.5	**7.3**
Volemitol	V'_2	**6.1**	20.1	12.5	11.4	**5.6**	19.8	11.5	10.1
	V'_1	8.8	20.7	11.1	**8.8**	7.9	20.2	10.2	**7.5**
Mean value ($\pm$ 1 ppm)									
E, A_1, M_1, G_1, V'_2		**6**	19	12	12	**6**	19	11	10
E, A_2, M_2, G_2, V'_1		8	20	10	**9**	7.5	19.5	10	**8**
Series E', tetradentate ligands of *ribo* or *altro* configuration									
Ribitol		**7.5**	16.9	9.3	13.8	**7.1**	16.7	8.3	12.7
D-Altritol [c]		7.5	17.3	10.1	12.7		ND		
Volemitol	V'_3	9.2	18.7	10.3	12.8	9.2	18.4	9.6	11.8
Mean value		8	17	10	13	8	18	9	13

[a] From Ref. [11]. [b] From Refs. [16], [17], and [25]. [c] From Ref. [18]. Data for volemitol were obtained in this study. When two complexes exist, the major one is identified by the subscript 1, the minor one by subscript 2, and the sites of chelation have been reversed to facilitate the comparison. Carbon atoms bearing primary hydroxyl groups are indicated in bold. The carbon atoms are given in consecutive order (for example: C-1,2,3,4 in erythritol), with the more deshielded one always placed in the second position. Ribitol $HOCH_2$ TTT CH_2OH D-Altritol $HOCH_2$ TTT CH_2OH Volemitol $HOCH_2$ TTT CH_2OH D-*glycero*-D-*manno*-heptitol



V_1 V_2

Fig. 2. Proposed structures for the ditungstate complexes of volemitol (V_1 and V_2, type E) showing the HO-1,2,3,4 tetradentate site occupied in two different orientations. The molybdate complexes V_1' and V_2' are similar. R = CHOH–CHOH–CH_2OH. In order to facilitate comparison, the complexes represented are those of the L enantiomer of volemitol (L-*glycero*-L-*manno*-heptitol).

sickle conformation. In such complexes, the less shielded tungsten atom (W-1) is bound to three consecutive oxygen atoms, whereas W-2 is bound to alternate oxygen atoms [25]. It indicates that W-1 is bound to three vicinal oxygen atoms of the ligand (O-2,3,4) and that W-2 is bound to O-1,2,4. A likely structure is represented in Fig. 2, showing the planar W-1–O-3–C-3–H-3 and W-2–O-1–C-1–H-1 arrangements responsible for the large (8–10 Hz) vicinal coupling constants.

In V_2, the W-1 atom was strongly coupled to H-2, whereas W-2 was strongly coupled to H-4 and weakly correlated with H-1. Knowing that V_1 and V_2 only differ by the reversed orientation of the site of chelation, it indicates that W-1 is bound to three vicinal oxygen atoms (O-1,2,3) and that W-2 is bound to O-1,3,4 (Fig. 2).

In V_3, the W-2 atom is strongly coupled to H-4, but the signal for W-1 could not be resolved. Such a phenomenon had been observed previously in the ^{183}W NMR spectrum of the tungstate–ribitol complex [25] (Table 3) and suggests a structural analogy between both species. Moreover, the same analogy was also noticed in the CIS patterns (^{13}C NMR) of the tungstate and molybdate complexes of volemitol (V_3 and V_3') and ribitol (Table 4). We assumed then that species V_3 and V_3' were isostructural with the tungstate and molybdate complexes of ribitol. Therefore, we assigned W-1 as being bound to O-3,5,6 and W-2 as being bound to O-3,4,5 (Fig. 3).

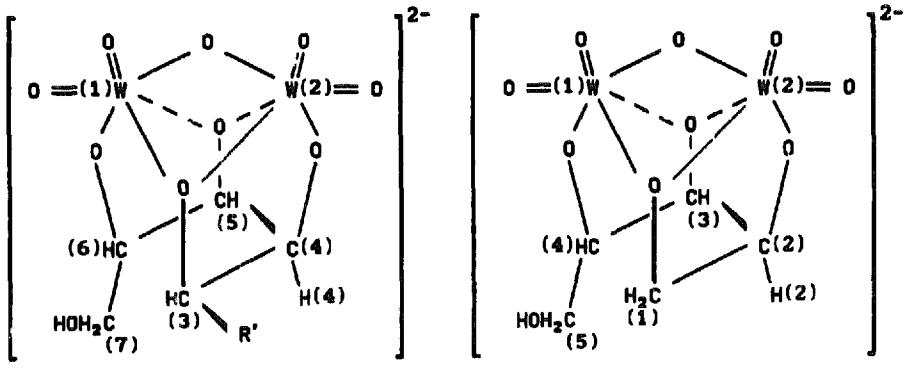


Fig. 3. Comparison of the proposed structures (type E') for the ditungstate complex V_3 of volemitol (left) showing the HO-3,4,5,6 site of chelation and the ditungstate complex of ribitol (right). The molybdate complex V_3' is similar to the tungstate species. R' = CHOH–CH_2OH.

4. Discussion

The NMR data prove unambiguously that the molybdate and tungstate complexes V_1–V'_1 and V_2–V'_2 (in which the site of chelation is the *arabino* system HO-1,2,3,4) are members of a structurally homologous series of complexes (series E) including those of erythritol, D-arabinitol, D-mannitol, and D-glucitol (Table 4). Their common structure has been established by analogy with those of the crystalline molybdate complexes of D-mannitol [8,9] and erythritol [10], that have been obtained by X-ray studies. A very characteristic NMR "fingerprint" is the large deshielding effect on one internal carbon, typically 18–21 ppm, while all other carbons are deshielded by less than 12.5 ppm. It has been ascribed [11] to a torsion of the corresponding carbon atom in order to accommodate the dinuclear metallic core.

A noteworthy point is that the proportions of complexes V_1 and V_2 are reversed with respect to other species of the series E. For example, the CIS patterns reported in Table 4 indicate conclusively that the major complexes V_1 and V'_1 of volemitol are related to the minor complexes A_2, M_2 and G_2 of arabinitol, mannitol and glucitol respectively [11].

Considering now the V_3 and V'_3 complexes of volemitol, it is found that chelation takes place at the HO-3,4,5,6 site, i.e., the site of chelation involves the *ribo* system (HO-4,5,6) and the internal neighbouring CHOH group HO-3 instead of the primary OH-7 group. The same phenomenon is observed [18,19] for D-altritol, in which the site of chelation is HO-2,3,4,5 and not HO-3,4,5,6. The finding that the CIS patterns are the same in the complexes of volemitol (V_3 and V'_3), altritol, and ribitol (Table 4) is in agreement with all species sharing a site of chelation of similar configuration. In the case of ribitol, this site involves the internal *ribo* system and the fourth ligating oxygen belongs necessarily to a CH_2OH group. Consequently, the complexes involving *ribo* and *altro* systems belong to the same series, designed as series E'.

Relative stabilities of type E and E' complexes.—The proportions of complexes reported in this study indicate that complexes V_3 and V'_3 (type E') are weaker than the *arabino* complexes (type E) of volemitol, although the latter involve a chelating primary hydroxyl group, which should decrease their stability. Whereas it is true for molybdate as well as for tungstate species, we will only discuss data for molybdate species in this paper (values for tungstate complexes are ca. 3 units higher). For example, the molybdate complexes of arabinitol (type E, $\log K_{212} = 16.35$) are stronger [11] than that of ribitol (type E', $\log K_{212} = 15.55$). K_{212} is the equilibrium constant of the complex-forming reaction and relates to the mean stability when a pair of isomeric complexes is formed:

$$2\,MoO_4^{2-} + H_nL + 2\,H^+ \leftrightarrows [(MoO_2)_2O(H_{n-4}L)]^{2-} + 3\,H_2O$$

Within a series of isostructural complexes, increasing the chain length of the alditol from $n = 4$ (tetritol) to $n = 6$ (hexitol) is known to be beneficial to the complex stability [27]. This effect was ascribed to the stepwise replacement of coordinating primary oxygen atoms by secondary (internal) oxygen atoms that become available as the chain length increases. It is most likely due to entropic gain since the participation of a CHOH group in the site of chelation is energetically favourable with respect to that of a terminal CH_2OH. In a previous paper [27], this gain per CHOH group was determined (from a plot of $\log K_{212}$ vs. n) to be close to $\Delta(\log K_{212}) \simeq 1.0$, equivalent to 2.5 kJ.mol^{-1} at 25°C. More recently, the cost

of restricting a rotor was evaluated by another method [28] and the value obtained was 2.6 ± 1 kJ.mol^{-1} per rotor. This excellent agreement justifies a tentative calculation of the formation constants of the complexes of volemitol and altritol.

For V'_3 and the complex of altritol, the site of chelation has the same structure as in ribitol ($\log K_{212} = 15.55$), but involves only CHOH groups. Replacing a CH_2OH group by a CHOH group should increase $\log K_{212}$ by ca. 1.0 unit, thus the formation constant for both molybdate complexes would be $\log K_{212} \simeq 16.5$. For the major species V'_1–V'_2, since the site of chelation is the *arabino* system HO-1,2,3,4 as in the mannitol and glucitol complexes of type E, the formation constants of all these species are probably close ($\log K_{212} \simeq 16.7$). The first conclusion is that complexes of type E, V'_1–V'_2, are indeed stronger than V'_3, in agreement with the experimental ratios (3:1). The second conclusion is that the mean formation constants would be $\log K_{212} \simeq 16.7$ for volemitol and $\log K_{212} \simeq 16.5$ for altritol.

The difference in stabilities between complexes of type E and E′ probably has a steric origin. Complexes of type E possess in their site of chelation a central *erythro* system surrounded by CH_2OH groups or CHOH groups in the *threo* orientation. Therefore, when lateral substituents are present, they are pushed away from the site of chelation (Fig. 2). On the contrary, in complexes of type E′, the site of chelation involves a *ribo* system, i.e., three vicinal CHOH group are in the *erythro* orientation. It locates the substituent borne by a lateral carbon atom in the vicinity of the site of chelation, creating then a steric interaction that destabilizes the complex with respect with type E (Fig. 3). It probably also modifies the torsion of the ligand that characterizes complexes of type E. Possible proofs of this steric strain in series E′ may be found in the reduced deshielding effect on the internal carbon atom of the site of chelation ($\Delta\delta$, 17 vs. 19–20 ppm) and in the lack of clear coupling between W-1 and H-6 (volemitol) or H-4 (ribitol), whereas such a coupling for W-1 is always observed in complexes of type E.

Another interesting difference between series E and E′ is that complexes of type E exist as isomeric pairs when the site of chelation bears two different lateral substituents [11], whereas only one complex of type E′ is formed with ribitol [11,25], D-altritol [18,19], or volemitol. Since the site of chelation of these ligands is not symmetrical, one must conclude that the second possible isomer is not formed, probably because it would be much weaker than the observed isomer.

The present results may help in understanding a study of the periodate oxidation of the molybdate complexes of volemitol [18]. Molybdate is expected to protect the bonds between the carbons involved in the site of chelation from cleavage by periodate. Free volemitol is oxidized to ribose (33%), arabinose (21%), altrose (15%), and mannose (11%), whereas in the presence of molybdate, its oxidation yields more altrose (20%) and mannose (15%), and less arabinose (18%) and ribose (13%). The clear decrease of the proportion of pentoses, associated with the increase in the production of hexoses, must be attributed to the formation of the tetradentate complexes that protect the HO-1,2,3,4 and the HO-3,4,5,6 systems, and induce cleavage of the C-6,7 and C-1,2 bonds. Finally, the high amount of oxidation products shows that volemitol is weakly bound to the molybdate group. For example, under identical conditions, the much more stable complex (of type E) formed with galactitol was oxidized in only 10% yield.

5. Conclusions

Volemitol forms three complexes with molybdate or tungstate ions. The pair of isomeric complexes involving the *arabino* HO-1,2,3,4 site of chelation in reversed orientations (type E) prevails over the third complex which involves the *altro* HO-3,4,5,6 site (type E′). A comparison of the latter species with the complexes of ribitol and D-altritol showed strong analogies that justify their grouping in the same type E′. The difference between types E and E′ lies in the orientation(s) of the side chain(s) borne by the carbon atoms at the extremities of the site of chelation. In complexes of type E, the side chains (if present) are pushed away from the site of chelation and no steric interaction occurs. On the contrary, in complexes of type E′, one side chain interacts with the site of chelation, which accounts for the lower stability and the absence of the second expected isomer.

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