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Evidence for molybdate complexes of ketoses and aldoses in the furanose form: a ^{13}C and ^{1}H NMR study

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ABSTRACT

The formation of dimolybdate complexes of ketoses of the *ribo* and *lyxo* series and of aldoses of the *lyxo* series was investigated by ^{13}C and ^{1}H NMR spectroscopy. All these sugars possess two *cis* hydroxyl groups adjacent to the anomeric centre and form two different series of complexes involving the furanose forms. The tridentate complexes of 2-ketoses involve the ring HO-3,4 and the *cis* exocyclic HO-1 of the β (*ribo* series) or of the α (*lyxo* series) anomer, whereas the *trans* anomeric HO-2 is not bound to molybdenum. In the *lyxo* series, the β anomers form tetradentate complexes involving HO-1,2,3,5 (aldoses) or HO-2,3,4,6 (ketoses), that appear similar to a β-D-lyxofuranose complex already characterized in the solid state. A mixture of tridentate and tetradentate species was obtained in the case of D-tagatose. The relative stabilities of the complexes are discussed.

INTRODUCTION

The discovery that molybdate ions catalyze the C-2 epimerization of aldoses in acidic media[1–7], allowing the preparation of rare sugars like D-lyxose, D- or L-ribose, and D-talose[8,9], renewed the interest in the chemistry of molybdate–carbohydrate complexes. These compounds are dinuclear species (Mo : sugar = 2) and the determination of their formation constants[10] by a potentiometric method[11,12] confirmed that sugars of the *lyxo* and *ribo* series[13] formed the more stable complexes. Structural studies of the ligands have been performed using ^{1}H and ^{13}C NMR[7,13–16], whereas ^{95}Mo NMR experiments[12,17] revealed the presence of two non-equivalent Mo atoms.

2-Ketoses do not epimerize like aldoses, but also form dimolybdate complexes that are expected to be structurally related to those of aldoses of the same series. In a recent study, Matulová and Bílik[18] reported that each of the four ketohexoses yielded two molybdate complexes: a common type of pyranose tridentate (HO-1,2,3) complex, and a second complex ascribed as tridentate pyranose species for D-taga-

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tose (HO-2,3,4) and D-psicose (HO-3,4,5), and as tetradentate species (HO-3,4,5,6) of the hydrated acyclic forms for D-fructose and L-sorbose.

In this work, a molybdate complex of a furanose form was unambiguously characterized by studying L-*erythro*-pentulose, a ketose that cannot adopt the pyranose form. Its complex displayed ^{13}C and ^{1}H NMR spectra related to those of complexes of D-psicose and D-tagatose[18], which prompted us to reinvestigate the structures of the complexes of these ketoses. Moreover, the spectrum of the second complex of D-tagatose (the ketose of the *lyxo* series) could also be assigned satisfactorily by assuming the sugar to be in the furanose form. Aldoses of the *lyxo* series were ultimately considered because a literature survey showed that a complex of β-D-lyxofuranose had been characterized in the solid state[19], whereas conflicting papers[7,10,13,14,16] claimed that D-lyxose and sugars of its series might complex molybdate in the pyranose form, either at the HO-1,2,3 or HO-1,2,3,4 site of chelation.

RESULTS

The complexes were prepared by mixing sodium molybdate, the ligand (L) and hydrochloric acid in D_2O, generally in stoichiometric proportions ($Mo:L:H^+ = 2:1:2$). The ^{13}C NMR spectra of the solutions showed signals attributed to the complex(es), in addition to those of the uncomplexed sugar. In principle, the complexation of molybdate induces variations ($\Delta\delta \simeq 5$–20 ppm) of the chemical shifts of the carbons of the site of chelation and increases their $^{1}J_{C,H}$ direct coupling constants. However, we had to compare with the furanose forms that are generally present in minute amounts in solutions of the free sugars. In such cases, the δ values were taken from the literature[20]. When a sugar formed two complexes, they were referred to by subscript 1 (major species) or 2 (minor species).

^{13}C NMR spectra, measured by us, were essentially in agreement with data for sugars that had already been studied by Bílik et al.[7,14,18]. However, we present evidence that assignments made for ligands considered as furanoses are more likely than those reported previously for pyranoses. Thus, it was necessary to reverse the C-1,6 assignments proposed earlier[18] in the case of D-tagatose. The proton spectrum of the D-psicose complex was completely assigned in this work, by referring to the much simpler spectrum of the L-*erythro*-pentulose complex.

L-*erythro*-Pentulose reacted readily with molybdate, as its ^{13}C NMR spectrum in the presence of molybdate showed the almost complete disappearance of the signals of the free ketose[21] (mixture of α-*f*, β-*f*, and acyclic forms). Two complexes in a 19:1 ratio were identified by the appearance of new signals. Three small signals were attributed to the minor species E_2 (δ 92.2–90.8–84.7 ppm), while the others could not be distinguished (probably buried in the CH_2 multiplet at 75–76 ppm). Species E_2 probably involves the acyclic sugar and resembles the ribitol complex[22,23] (Table I). The C-2 carbonyl group is probably hydrated as no signal for the ketonic carbon was found above 200 ppm.

TABLE I

^{13}C NMR chemical shifts [a] (δ in ppm) and coupling constants ($^{1}J_{C,H}$ in Hz) of ketoses and the type K molybdate complexes

Sugar	Carbon [b]					
	C-1	C-2	C-3	C-4	C-5	C-6
L-*erythro*-Pentulose						
Complex E_1	75.3	112.0	90.1	83.2	76.2	
$^{1}J_{C,H}$	148		154	159	150	
u, α-*f*	65.5	105.2	74.1	73.1	72.8	
u, β-*f*	65.2	108.3	78.4	73.3	73.4	
u, keto	69.1	215.2	78.0	75.3	64.0	
u, hydrate [c]	66	99	75	72	64	
$\Delta\delta$ / α-*f*	9.8	6.8	16.0	10.1	3.4	
$\Delta\delta$ / β-*f* [d]	10.1	3.7	11.7	9.9	2.8	
$\Delta\delta$ /hydrate	9.3	13.0	15.1	11.2	12.2	
Ribitol complex [e]	72.1	91.0	83.7	87.9	63.9	
D-Psicose						
Complex P_1	74.2	110.8	88.0	82.8	87.9	63.2
$^{1}J_{C,H}$	148		152	158	152	143
u, α-*p*	64.0	98.5	66.4	72.6	66.7	58.8
u, β-*p*	64.9	99.2	71.2	66.0	69.9	65.0
u, α-*f*	64.2	104.1	71.2	71.2	83.5	62.2
u, β-*f*	63.3	106.5	75.6	71.9	83.5	63.7
$\Delta\delta$ / α-*p* [f]	10.2	12.3	21.6	10.2	21.2	4.4
$\Delta\delta$ / β-*p*	9.3	11.6	16.8	16.8	18.0	−1.8
$\Delta\delta$ / α-*f*	10.0	6.7	16.8	11.6	4.4	1.0
$\Delta\delta$ / β-*f* [d]	10.9	4.3	12.4	10.9	4.4	−0.5
D-Tagatose						
Complex T_2	73.3	110.4	88.3	81.3	83.5	62.4
u, α-*p*	64.8	99.0	70.7	71.8	67.2	63.1
u, β-*p*	64.4	99.1	64.6	70.7	70.1	61.0
u, α-*f*	(64.0)	105.7	77.6	71.9	80.0	(63.0)
u, β-*f*	63.5	103.3	71.7	71.8	80.9	61.9
$\Delta\delta$ / α-*p*	8.5	11.4	17.6	9.5	13.4	−0.7
$\Delta\delta$ / β-*p* [f]	8.9	11.3	23.7	10.6	13.4	−1.4
$\Delta\delta$ / α-*f* [d]	(9.3)	4.7	10.7	9.4	3.5	(−0.6)
$\Delta\delta$ / β-*f*	9.8	7.1	16.6	9.5	2.6	0.5

[a] In D_2O, reference sodium 4,4-dimethyl-4-silapentane-1-sulfonate by the substitution method[22]. u: assignments for uncomplexed sugars according to refs. 20 and 21. Values in parentheses were not given in the literature and were estimated from data for related sugars. δ values ± 0.1 ppm; J values ± 1 Hz. [b] Carbons appearing in the same column are structurally equivalent. [c] Estimated values (± 1 ppm) by reference to ketoses[18] and hydrated erythrose and threose[20]. [d] Proposed structure (this work) for the complexed ligand. [e] Literature data[22,23]. [f] Proposed structure in ref. 18.

^{13}C NMR chemical shifts and $^{1}J_{C,H}$ coupling constants for the signals of the major complex E_1 are displayed in Table I. Assignments were made from a 2D (^{1}H–^{13}C) XHCORR experiment. The ^{1}H NMR spectrum was completely assigned

TABLE II

^{1}H NMR chemical shifts (δ in ppm) and coupling constants ($J_{H,H}$ in Hz) of ketoses and the type K molybdate complexes [a]

Sugar	Proton							
	H-1	H-1′	H-2	H-3	H-4	H-5R	H-5S	
L-*erythro*-Pentulose								
u, α-*f* [b]	3.59	3.55		4.13	4.34	4.03	3.93	
u, β-*f* [b]	3.75	3.64		4.11	4.54	4.19	3.77	
u, *keto* [b]	4.69	4.54		4.38	3.97	3.68	3.64	
Complex E_1	4.22	4.10		4.84	4.76	4.07	3.99	
	$J_{1,1'}$	$J_{3,4}$	$J_{4,5R}$	$J_{4,5S}$	$J_{5R,5S}$			
u, α-*f* [b]	12.0	5.3	4.8	2.8	10.1			
u, β-*f* [b]	11.9	4.9	5.9	4.8	9.5			
u, *keto* [b]	19.5	5.4	6.3	5.2	11.6			
Complex E_1	8.45	3.6	1.6	w	10.35			
	H-1	H-1′	H-2	H-3	H-4	H-5	H-6	H-6′
D-Psicose								
Complex P_1	4.26	4.20		4.95	4.63 [d]	4.31	3.65	3.57
Complex P_1 [c]	4.18	4.18		4.91	4.62	4.15	3.60	3.60
	$J_{1,1'}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$		
Complex P_1	8.45	3.85	w	4.9	4.9	13.8		

[a] In D_2O, accurate to ± 0.01 ppm and ± 0.1 Hz. H-5 are designated[21] by R if *cis* to H-4 and S if *trans* to H-4. [b] u: uncomplexed ligand, assignments from ref. 21. [c] Literature data[18]. For D-tagatose[18], only values for H-3 (δ 4.84) and H-4 (δ 4.69) were reported. [d] Signal overlapping with the HOD peak ($\delta \pm 0.06$ ppm). Values of $J_{3,4}$ were reported[18] for the D-psicose (3.9 Hz) and the D-tagatose (3.6 Hz) complexes. w: less than 0.2 Hz.

by a homodecoupling process (Table II). The structure of the complexed ligand was determined as follows. The absence of any signal above 200 ppm ruled out the presence of an acyclic, carbonyl form. Furthermore, the ^{13}C NMR spectrum differed from those of complexes of comparable ligands known to be in the acyclic form, such as D-arabinitol or ribitol[22,23]. Moreover, if L-*erythro*-pentulose had been complexed in a hydrated, acyclic form, all carbons would appear deshielded by at least 9 ppm (Table I), suggesting a very unlikely pentadentate site of chelation. As the ligand could not adopt the pyranose form, the conclusion could only be that we were dealing with a complex of a furanose form.

Whether the configuration was α or β was deduced from structural considerations. Assuming the sugar to be in α-*f* form, the variations of ^{13}C chemical shifts (all $\Delta\delta > 5$ ppm except for C-5) would point to the characterization of a tetradentate (HO-1,2,3,4) species. Such a result is unlikely, because HO-1 and HO-2 are located on opposite sides of the ring, making it difficult to imagine how the HO-1 group could be bound to Mo ($\Delta\delta$ 10.7 ppm) in conjunction with the *cis* system HO-2,3,4. On the contrary, if the sugar is complexed in β-*f* form, HO-2 is not involved in chelation ($\Delta\delta$ 3.7 ppm only) and the chelating HO-1 group ($\Delta\delta$ 11 ppm) is located *cis* to the HO-3,4 system. The proton spectrum confirms that the

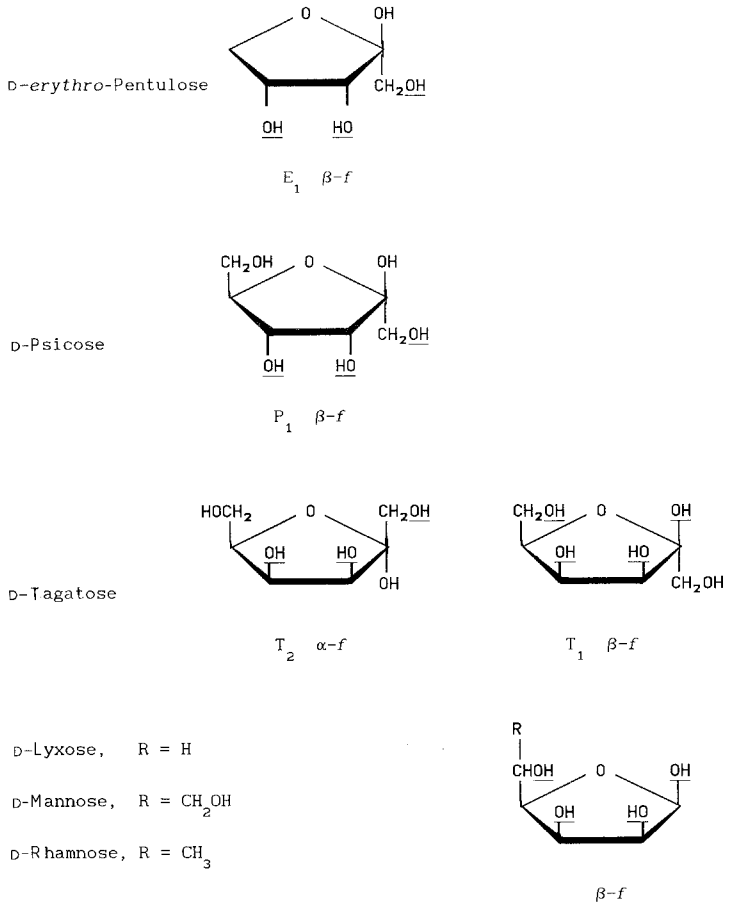

Fig. 1. Furanose structures of the sugars in their molybdate complexes. The homologous series are arranged into columns, corresponding to the tridentate complexes of the type K series (left) and to the tetradentate complexes of the *lyxo* series (right). Underlined HO groups belong to the site of chelation. For the sake of clarity, D-*erythro*-pentulose is shown instead of the L enantiomer.

site of chelation involves HO-1,3,4, but not HO-5, as the proton signals of the complexed CH_2OH group are clearly shifted ($\delta \simeq 4.2$–4.1, instead of 3.7–3.6 in uncomplexed furanoses[24]). Thus NMR data support the conclusion that the major complex E_1 is a tridentate complex (HO-1,3,4) of the *β-f* form (Fig. 1).

D-*ribo*-Hexulose (D-psicose), forms two complexes in a 9:1 ratio, in agreement with literature data. The minor P_2 species has been reported[18] to be homologous to the major complex of D-ribose, and the present discussion will be limited to the major P_1 species, which has been considered by Matulová and Bílik as a tridentate complex (HO-1,2,3) of the *α-p* form[15]. However, if we adopt this hypothesis, the $\Delta\delta$ values calculated in Table I indicate that all carbons from C-1 to C-5 are deshielded, which disagrees with the proposed tridentate site of chelation. The same conclusion applies to the *β-p* form.

Another possible interpretation was the complexation of the hydrated, acyclic form of the ligand (the ketonic form was ruled out in the absence of signals above 200 ppm). Such complexes have been reported[18] for other ketoses, namely D-fructose and L-sorbose, and for the E_2 species described here. The ribitol complex was retained as a possible model for such a species and its spectrum was compared to that of P_1, but the hypothesis was dismissed for the same reasons as those given for L-*erythro*-pentulose.

D-Psicose was suspected to be complexed in the furanose form on the basis of the analogy of its NMR spectra with those of L-*erythro*-pentulose (Tables I and II), and of the characteristic value of the chemical shift (δ 87.9) for C-5. As HO-5 cannot be complexed if involved in the formation of the furanose ring, a small $\Delta\delta$ value would be expected for this carbon (found: $\Delta\delta$ 4.4). The variations of carbon chemical shifts induced by complexation are given in Table I and display a pattern comparable to that for L-*erythro*-pentulose. The same analogy holds for the values of the coupling constants. Because similar structures may be assumed for both complexes, D-psicose must be complexed in the β-*f* form with a tridentate HO-1,3,4 site of chelation.

The respective assignments to C-1 and C-6 of the 74 and 63 ppm signals in the spectrum of the complex were in agreement with the ^{1}H NMR spectrum, which showed clearly that C-1 belonged to the site of chelation, because the H-1,1′ signals ($\delta \simeq 4.2$) were shifted, in contrast to H-6,6′ ($\delta \simeq 3.6$). These results agreed with structural evidence that HO-6 was not a likely chelating group because it was oriented *trans* to the HO-3,4 system, whereas HO-1 was *cis*. Consequently, as in L-*erythro*-pentulose, the anomeric HO-2 *trans* to HO-1,3,4 is not considered to be involved in the chelation site of β-D-psicofuranose.

The ^{1}H NMR spectrum of complex P_1 was completely assigned and compared to the spectrum of the E_1 species (Table II). The involvement of an exocyclic CH_2OH group in the site of chelation induces a characteristic decrease of the corresponding $J_{H,H}$, coupling constants (8.45 Hz for H-1,1′ vs. 13.8 Hz for H-6,6′ and $\simeq 12$ Hz for uncomplexed CH_2OH groups[24]). As for the ^{13}C NMR spectra, the remarkable matching conclusively attests the close analogy between the structures of both complexes.

D-*lyxo*-Hexulose (D-tagatose), forms two species T_1 and T_2 in a 7:3 ratio. The structure of the major species T_1 is homologous to the complexes of the aldoses of the *lyxo* series and is discussed hereafter. The minor complex T_2 has been described[18] as a tridentate (HO-1,2,3) species of the β-*p* form. In fact, its ^{13}C NMR spectrum is undoubtedly related to those of the ketose complexes characterized here and agrees with the ligand being in the α-*f* form (δ 83.5 for C-5) chelating with the HO-1,3,4 system (Table I). The α configuration agrees with HO-1 being *cis* to the HO-3,4 groups. However, both C-1 and C-6 bear a hydroxyl group *cis* to HO-3,4, but the involvement of HO-6 was not considered possible because, if it were the case, similar complexes would be formed by other *lyxo*

TABLE III

^{13}C NMR chemical shifts (δ in ppm) of sugars of the *lyxo* series and of the *lyxo* molybdate complexes

Sugar	Carbon [a]					
D-Tagatose	C-1	C-2	C-3	C-4	C-5	C-6
Complex T_1 [b]	65.2	119.9	84.9	87.6	82.4	68.2
$\Delta\delta/\alpha$-*p*	0.4	20.9	14.2	15.8	15.2	5.1
$\Delta\delta/\beta$-*p* [c]	0.8	20.8	20.3	16.9	12.3	7.2
$\Delta\delta/\alpha$-*f*	1.2	14.2	7.3	15.7	2.4	5.2
$\Delta\delta/\beta$-*f* [d]	1.7	16.6	13.2	15.8	1.5	6.3
D-Lyxose						
Complex [e]	112.8	84.1	87.7	81.2	68.5	
u, β-*f*	96.3	73.2	71.0	82.1	62.7	
$\Delta\delta/\beta$-*f*	16.5	10.9	16.7	−0.9	5.8	
D-Mannose						
Complex [e]	112.2	84.1	88.3	79.7	79.3	64.8
u, β-*f*	96.6	73.1	71.2	80.7	71.0	64.4
$\Delta\delta/\beta$-*f*	15.6	11.0	17.1	−1.0	8.3	0.4
L-Rhamnose						
Complex [e]	112.3	84.5	89.0	83.8	75.6	23.3
u, β-*f*	96.6	73.1	71.4	85.7	67.0	20.0
$\Delta\delta/\beta$-*f*	15.7	11.4	17.6	−1.9	8.6	3.3

[a] In D_2O, reference sodium 4,4-dimethyl-4-silapentane-1-sulfonate by the substitution method[22]. Carbons appearing in the same column are structurally equivalent. u: assignments for uncomplexed sugars according to ref. 20. Chemical shifts for uncomplexed D-tagatose are given in Table I. δ values ± 0.1 ppm; J values ± 1 Hz. [b] Values in agreement with ref. 18, except for C-1 and C-6 that were reversed on the basis on analogy within the series. [c] Proposed structure for the complexed ligand in refs. 10 and 18. [d] Proposed structure (this work). [e] From ref. 10.

aldoses with homologous sites of chelation (HO-2,3,5), contrary to the experimental behaviour that is presented hereafter.

Thus, the experimental results point to the three 2-ketoses forming a homologous series of furanose complexes (type K series, Fig. 1) in which the exocyclic HO-1 is part of the tridentate site of chelation, together with the ring *cis* HO-3,4 groups. In contrast, the anomeric HO-2 is not complexed, as it is located *trans* to the site of chelation.

The major complex T_1 of D-tagatose was previously described[18] as a tridentate (HO-2,3,4) β-*p* species. However, when the corresponding $\Delta\delta$ values are calculated (Table III), the four carbons C-2 to C-5 appear deshielded by 21–12 ppm, making it difficult to understand why C-5 would be highly deshielded ($\Delta\delta$ 12.3) if it is not involved in the site of chelation. On the other hand, this result is in agreement with data reported for a series of *lyxo* aldoses (D-lyxose, D-mannose, and L-rhamnose) by Verchère and Chapelle[10], who claimed that the site of chelation involved the HO-1,2,3,4 groups, homologous with HO-2,3,4,5 of D-tagatose. Nevertheless, such tetradentate species are structurally unrealistic because it is unlikely that the dimolybdate group can be accommodated by the proposed site, in which the distance between the extreme oxygen atoms is much too large. In

conclusion, although *lyxo* sugars, including D-tagatose, are complexed beyond doubt in the β form[10,14,18], it appears that neither of the proposed structures involving the ligands in β-*p* form can satisfactorily agree with NMR and structural data.

The suggestion that the major complexes of the *lyxo* sugars probably involve their furanose forms came from the above examples of ketose complexes, and from the report[19] that D-lyxose had been characterized in β-*f* form (HO-1,2,3,5 site) in a molybdate complex isolated in crystalline form. Accordingly, when the $\Delta\delta$ values were recalculated for the four sugars in β-*f* forms (Table III), all carbons showed variations of chemical shifts in agreement with the above tetradentate site of chelation. In particular, C-4 (aldoses) or C-5 (ketoses), which have no available hydroxyl group, were almost not deshielded. Moreover, these $\Delta\delta$ values were nicely consistent for structurally equivalent carbons within the series, as expected because of the close analogy between the sites of chelation (HO-2,3,4,6 for tagatose and HO-1,2,3,5 for aldoses). It prompted us to reverse the assignments proposed earlier[18] for C-1 and C-6 in the T_1 species, in order to get a complete agreement for the $\Delta\delta$ values in the whole series.

It can be concluded that, despite repeated reports, sugars of the *lyxo* series do not form molybdate–pyranose complexes. ^{13}C NMR data are in better agreement with the tetradentate furanose structures[19], already characterized in the solid state. The corresponding *lyxo* series of complexes is illustrated in Fig. 1.

DISCUSSION

This work presents evidence that two different series (type K and *lyxo*) of molybdate complexes involve sugars in the furanose form and not in the usual pyranose form. This disagreement with earlier literature warrants some further comments.

For 2-ketoses, previous work[18] is limited to one study, by ^1H and ^{13}C NMR, that did not determine the variations of chemical shifts arising from the complexation. The structures of the complexes were proposed from structural considerations, with the assumption that the site of chelation (HO-1,2,3) must possess three hydroxyl groups in *eq–ax–eq* conformation. The data presented in Tables I and II show the better quality of the treatment made with our hypothesis. Moreover, the new results obtained in the case of L-*erythro*-pentulose that cannot adopt the pyranose form, conclusively attest the existence of complexes of ketoses in the furanose form.

The case of the *lyxo* aldoses and ketose is not so obvious, as several studies pointed towards the complexation of the pyranose form either in tridentate (HO-1,2,3) or tetradentate (HO-1,2,3,4) complexes. Earlier, we pointed out how the assumption that ligands are pyranoses conflicts with the NMR and structural data. Previous studies were probably influenced by earlier papers of Weigel et

al.[25,26] emphasizing the need for four *vicinal* hydroxyl groups in molybdate complexes. Although it is true in the alditol series[22,23], the crystal structure[19] of the D-lyxofuranose complex demonstrates that sugars in cyclic forms may chelate with molybdate through four *cis* hydroxyl groups that are not vicinal.

The relative stabilities of complexes of both types may be compared in the case of D-tagatose, as the *lyxo* species T_1 is more stable than the type K species T_2 (7:3). However, in the case of D-psicose, the type K species P_1 is strongly favoured with respect to the *ribo* species P_2 (9:1). It suggests the following sequence of stabilities: *lyxo* > type K > *ribo*.

Although few thermodynamic data are available for molybdate complexes of sugars, there is general agreement that sugars of the *lyxo* series form more stable complexes than those having any other configuration. It would suggest that the *lyxo* tetradentate complexes are specifically more stable than the *ribo* cyclic complexes and the acyclic complexes formed in the *arabino* and *xylo* series[7]. Thus, the structure of the *lyxo* ligands must possess a peculiar character that is absent in the *ribo* series. As such, the most important difference between the furanose forms appears to be the relative orientation of the HO-5 or -6 group, which is *cis* in the *lyxo* series and *trans* in the *ribo* series. It indicates that only *lyxo* compounds can achieve extra stabilization by forming a fourth coordinating bond with this *exocyclic* hydroxyl group.

It is also interesting to discuss the relative stabilities of the various possible sites in the case of D-tagatofuranose (Fig. 1). No evidence was found for a complex with a site of chelation involving HO-3,4 and both exocyclic HO-1 and HO-6, probably because of inadequate geometry for accommodation of the dimolybdate group. The β isomer gives the HO-2,3,4,6 *lyxo* complex, whereas the α isomer gives only the HO-1,3,4 type K complex and not the plausible HO-3,4,6 complex of comparable structure. It can be related to a higher reactivity of HO-1 that is nearer the anomeric centre at C-2. Apparently, HO-5 (aldoses) or HO-6 (ketoses) is complexed only when it can form the fourth bond of a complex already involving three hydroxyl groups. A lower strength for this bond is suggested by the smaller deshielding effect of molybdate on C-5 or C-6 in the *lyxo* series ($\simeq$ 6 ppm for CH_2OH and $\simeq$ 8.5 ppm for CHOH) as compared to the exocyclic C-1 in the type K series ($\simeq$ 10 ppm). It may indicate a smaller loss of freedom of the CH_2OH group in the tetradentate *lyxo* complexes as compared to the tridentate type K complexes.

Support for our conclusion is provided by recent results obtained for aldotetroses, that cannot exist in the pyranose form. It was established[27] that D-erythrose and D-threose were unable to form molybdate complexes in their cyclic furanose form, contrary to a previous report[28], but were complexed in their hydrated acyclic forms. It demonstrates clearly, at least in the case of D-erythrose, that the hypothetical complex involving the *cis* HO-1,2,3 of the α-*f* form would have a lower stability than the tetradentate (HO-1,2,3,4) site of the acyclic form. It confirms the rule that the chelation of molybdate by a furanose ring possessing two

or three vicinal *cis* hydroxyl groups should require the participation of one exocyclic CH(R)OH group.

EXPERIMENTAL

Commercial sugars and all other chemicals were of analytical grade and used as supplied. Water was de-ionized in a Millipore apparatus.

For the preparation of the complexes, we did not use the classical procedure[18] of adding the sugar to a solution of ammonium heptamolybdate. The molybdate source was disodium molybdate dihydrate and the solutions were acidified with concd HCl. This technique allows slight variations of the initial ratios and of the pH which modify the relative proportions of the complexes at equilibrium. It sometimes facilitates the identification of the signals corresponding to each species.

All 1D and 2D NMR spectra were recorded with a Bruker AM 360 spectrometer equipped with a 5-mm multinuclear probe.

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