

ISSN 0011-1643

UDC 541.124

CCA-2017

Original Scientific Paper

Heptamolybdate Ion Catalyzed Epimerization of Monosaccharides. CD Study of Binding of Monosaccharides and Polyols to Molybdate and Tungstate

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Received October 9, 1991

Conformational properties and weak interactions of monosaccharides in the oxo-complexes with ammonium heptamolybdate (AHM) and ammonium paratungstate (APT) are studied by the CD spectroscopy, and their relation to the catalytic C(2) epimerization step is discussed. It is found for molybdate complexes that there is unequivocal correlation between the torsional angles around the 1,2,3-triol subunit in the bound monosaccharide and the Cotton effects between 325 and 300 nm, 286 and 260 nm, and that around 235 nm. A positive torsional angle in 1,2-*cis*-2,3-*cis* triols leads to a positive first and second, and a negative third mentioned Cotton effect. Assuming a 1:2 ratio for the monosaccharide to Mo(VI) in the complex, as strongly indicated by a recent ⁹⁵Mo-NMR study, binding in the ¹C₄ conformation can be predicted for the monosaccharides from the *lyxo*-series, whereas for those of *ribo*-series binding in ⁴C₁ conformation predominates. The first type of hexoses seems to engage the C(6)H₂OH group, if present, whereas the second one binds *via* 1,2,3-OH groups in *cis*-configuration. The absence of CD effects with the cyclic polyols 1-6, derived from various pyranoses, revealed that either three OH groups with *cis*-configuration or two *cis*-hydroxy groups and an *axially* arranged *cis*-CH₂OH group represent the minimal structural requirement for the formation of the CD active oxo-complexes. Two hexitols, D-glucitol 7, and D-mannitol 8, also form 1:2 complexes, engaging four hydroxy groups »from the end« of the chain (C(6)-C(3)), as found by the X ray analysis for the crystalline complex of D-mannitol. This complexation mode leaves unbound C(2), the only chiral center with the opposite configuration in these two ligands, leading to very similar CD spectra of the two complexes.

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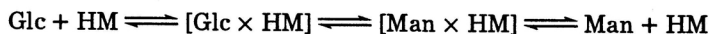
With ammonium paratungstate (APT) D-Man (10) and D-Lyx (16), but not D-Glc (9) and D-Xyl (15), gave a CD active complex, with all Cotton effects ca. 5–10 times more intensive and strongly hypsochromically shifted (for ca. 30–40 nm) as compared to their AHM complexes. Similar enhancement of intensity and hypsochromic shifts were also observed for the APT complexes of the two hexitols 7 and 8. Whereas APT with disaccharide D-maltose (18) gave no CD, D-maltitol (19) exhibited nearly enantiomorphic CD curve to the former hexitols, with very large Cotton effects, e.g. $\Delta\epsilon + 72$ at 203 nm. This relation of the CD curves can be explained by the different binding regions for 19 and for 7 and 8. The former is presumably bound *via* C(1)–C(3) sequence, which may adopt the conformation enantiotopic to that in the binding region of 7 and 8.

Most surprising, however, is the complete absence of the catalytic effect of APT on C(2) epimerization of D-Glc, D-Man, D-Xyl, and D-Lyx. This can be explained by different degrees of M---O $d\pi$ - $p\pi$ interaction in two isopolyanions. The tungstate anion seems to be less effective in stabilizing, *via* back-donating interaction, the partially positive charge on C(1) in the complexed aldoses, which seems to be the prerequisite for the rearrangement that leads to C(2) epimerization.

INTRODUCTION

The heptamolybdate (HM) ion catalyzed epimerization of sugars at the C(2) atom is of great practical importance, and several proposals relating to the mechanism of this reaction have been published.²⁻⁵ In the course of our study of the HM ion catalyzed C(2) epimerization of D-glucose (D-Glc, 9), and D-mannose (D-Man, 10), we became interested in the events that precede the strong $d\pi$ - $p\pi$ interaction proposed for the catalytic step.^{4,5} To this aim we have reinvestigated the chiroptical (CD) properties of some monosaccharide- and polyol-complexes with (poly)molybdate, and for the first time determined the CD spectra of their complexes with (poly)tungstate. Formation of such oxo complexes represents the first, weak interaction of a monosaccharide with the »pre-catalyst«, the actual catalytic species being unknown as yet. According to the most recent results, dimolybdate $\text{Mo}_2\text{O}_7^{2-}$ seems the probable species that binds monosaccharides at ambient temperature forming rather stable oxo-complexes.⁶⁻¹⁰ Since pre-organization of the ligand is one of the first principles of tight binding,¹¹ the binding is stronger the more the conformation of the free monosaccharide resembles that of the bound one. By the same token, the more similar the conformation of the monosaccharide in the oxo-complex is to that in the catalytic complex, the faster epimerization can be expected.

If a reversible monosaccharide-HM complex is formed prior to the rearrangement of the bonds in the course of epimerization, the following minimal reaction mechanism can be proposed:



Some data about the rates and activation energies of the single steps are available. Michaelis constants K_m for D-Glc→D-Man, and for D-Man→D-Glc, *i.e.* for the forward and reverse reactions, are found to be $(73 \pm 3) \times 10^{-3}$ M, and $(5.3 \pm 0.7) \times 10^{-3}$ M, respectively.⁵ The activation energies of these processes are ca. 96 and 99 kJ/mol. respectively.⁵ Standard free energy differences ΔG^\ddagger obtained upon complexation of these two

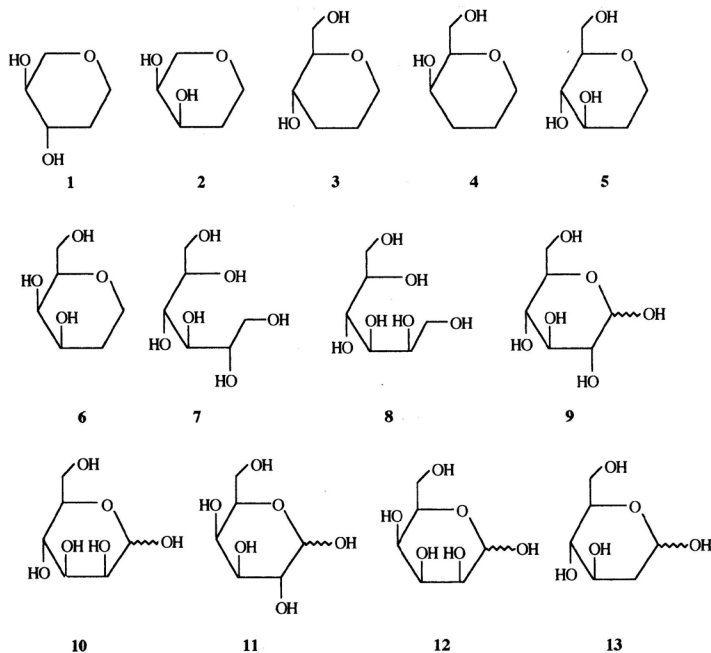
monosaccharides with HM are -7.8 , and -15.6 kJ/mol for [Glc x HM] and [Man x HM], respectively.⁵ The formation constant, expressed as $\log K$, for [Man x HM] is found to be 14.5 , a similar value is found for D-lyxose (D-Lyx, 16).⁷ No data are cited for their-ribo-congeners D-Glc and D-Xyl (15).

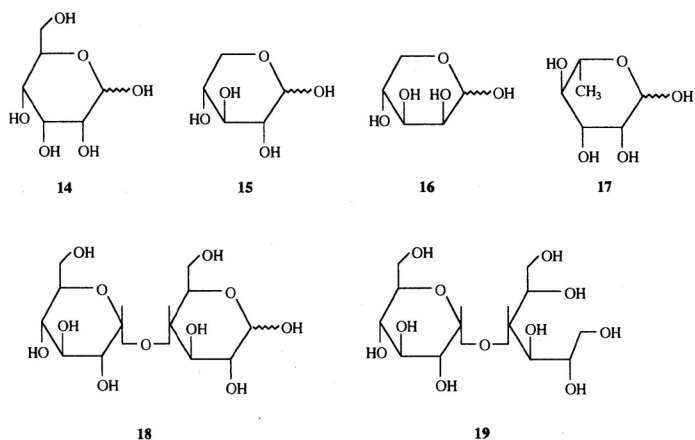
Previous studies afforded some insight into the conformation of the monosaccharides bound to (poly)molybdate. Studies in the solution were performed by CD,¹²⁻¹⁴ potentiometry,^{7,15} and ¹³C- and ⁹⁵Mo-NMR spectroscopy.⁶⁻⁹ The solid state structure was determined by X-ray analysis of the crystalline complexes of dimolybdate with D-lyxose (16),¹⁶ D-mannitol (8),¹⁷ and erythriol.¹⁸ No CD study of binding of monosaccharides to (poly)tungstate is reported, the only data for the complexes have been obtained by NMR spectroscopy⁶ and potentiometry.⁷

RESULTS AND DISCUSSION

In our present study, we were able to measure with more modern equipment the CD-spectra of some monosaccharides (9-17) over a greater wavelength range, and we included also some chiral, cyclic and acyclic, diols, triols and hexitols (1-8). all derived from monosaccharides

The concentrations of the monosaccharide and the molybdate used in the early CD study by Voelter *et al.*^{13,14} were much higher than those we used, and we even had difficulties to get clear solutions with approx. 1:10 of the amount of monosaccharide. For two Cotton effects of the complex with D-Man (10) we determined, therefore, the heptamolybdate concentration-dependence of the differential absorbance DA, and linearity was found in the concentration range up to ca. 2 mmol/L. At higher concentrations, DA approaches asymptotically a constant value (Figure 1.)





All our measurements with molybdate and tungstate were then performed with concentrations so as to remain in this linear range. It is important to note, however, that this concentration range of isopolyanions (1–2 mmol/L), and of the ligands (2 mmol/L), is much lower than that used in the NMR experiments^{6,8,9} (ca. 500 mmol/L of AHM or APT and ca. 1500 mmol/L of the ligand).

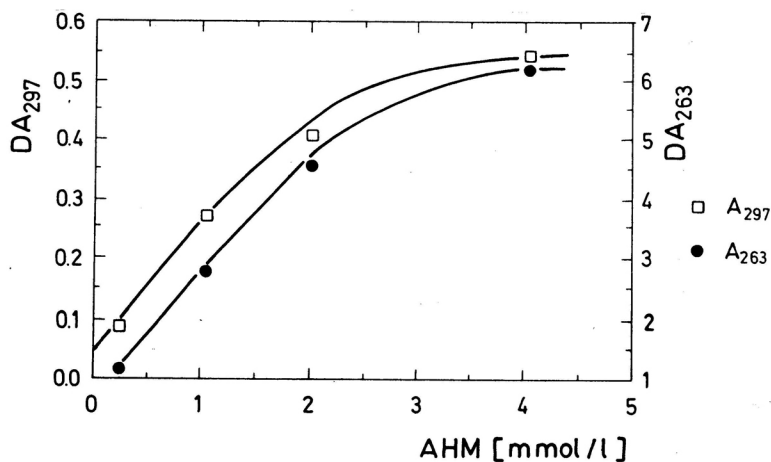


Figure 1. Plot of differential absorption (DA, absolute values) at 263 nm and 297 nm of the complex molybdate-D-Man (10) vs. concentration of ammonium heptamolybdate (AHM). The concentration of D-Man was 2.0 mmol/L.

CD Spectra of the Complexes with Molybdate

On the basis of the earlier CD measurements it was concluded¹²⁻¹⁴ that aldoses with a *trans*-arrangement at C(2) and C(3) give two CD-bands of the opposite sign, one between 280–270 nm and the other around 245 nm. The sign of the first band is the

same as the sign of the torsional angle between the two OH groups at C(2) and C(3), the sign of the second band, which is usually much stronger, is opposite to the first one. For *cis*-2,3 diols, usually three Cotton effects could be found; the first very small one around 300 nm, the second between 272–262 nm, and the third, which is usually the biggest, between 237–230 nm.

All three CD bands of the D-Man complex are shifted hypsochromically from their positions in *e.g.* the D-Glu (Figure 2). On the other hand, for the complexes of the selected acyclic polyols D-glucitol (7) and D-mannitol (8), the usual band positions were observed (Figure 3). From the CD-signs follows that in the complexes of monosaccharides with a 2,3-*cis* diol moiety, a methyl group C(6) always adopts the equatorial conformation, as does the CH₂OH group when it is in *trans* arrangement to the two OH groups at C(2) and C(3). However, in the cases where these OH groups are on the same side of the ring, *i.e.* in *ribo*-configuration, additional complexing with the axially arranged CH₂OH moiety seems possible, which could stabilize the ¹C₄ conformation in these complexes (Scheme 1.)

D-Man gave the small first Cotton effect, but it was also observable for D-Glu (9) and D-galactose (D-Gal, 11), as well as the two hexitols, (7) and (8) (Figures 2 and 3.)

In their second paper¹⁴, the authors published the CD-curve of the D-Gal (11) complex, and found also this small first Cotton effect, but did not comment on it. It seems, therefore, that in all cases the first Cotton effect appears, but it may easily be overlooked if it has the same sign as the second one, as for D-Glu, D-Xyl, and D-glucitol. In addition to these three bands, a fourth one could be detected around 210 nm, whose effect is somewhat smaller than that around 240 nm. For D-glucitol, the first band has the same sign as the second and is, therefore difficult to detect, whereas these two

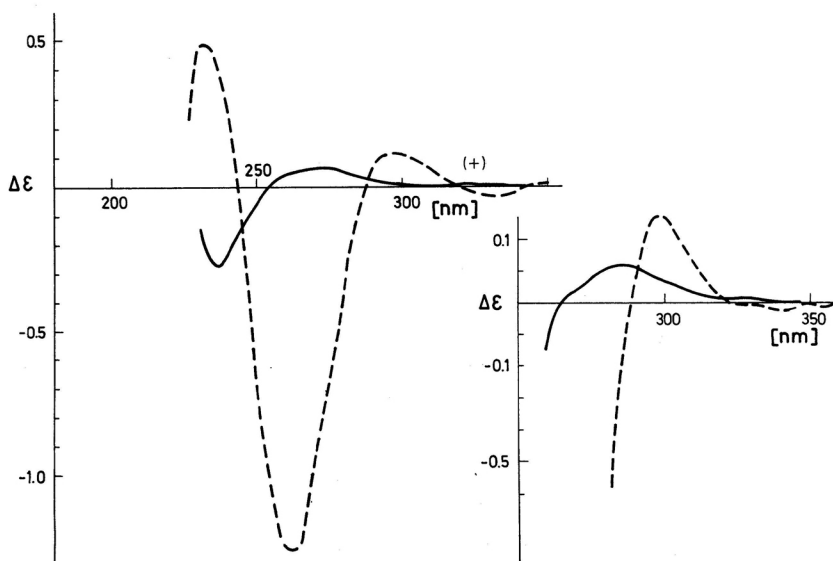


Figure 2. CD Spectra of molybdate complex of D-Glc (9,—) and D-Man (10,---).

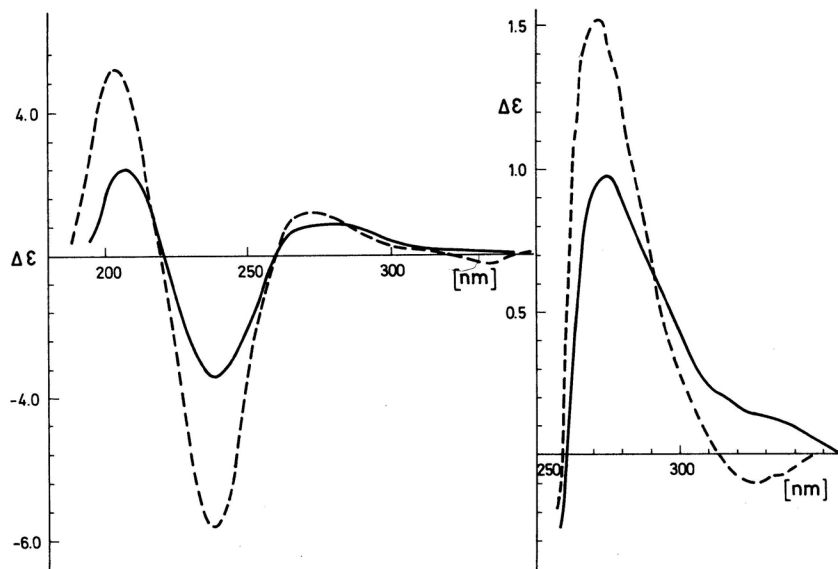
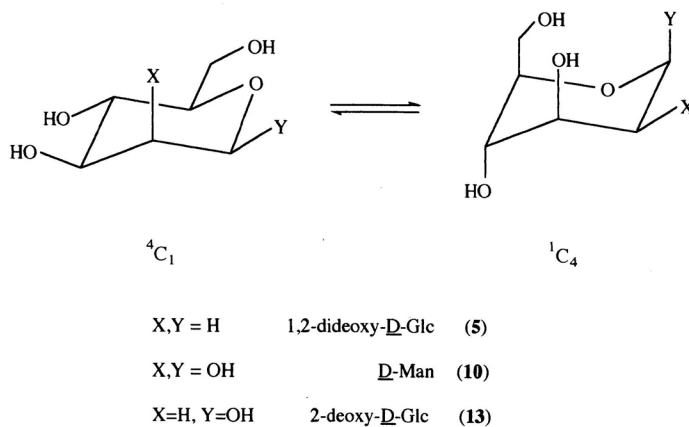


Figure 3. CD Spectra of molybdate complex of D-glucitol (7,—) and D-mannitol (8,---).



SCHEME 1

bands have opposite signs for D-mannitol. Also, some »saturation« is observed for these two compounds, *i.e.* no linear dependence of the Cotton effects from the polyol-to-molybdate ratio.

In the complex of 2-deoxy-D-glucose (13) a CD was found¹⁴ although this compound lacks the OH group at C(2). If this molecule is complexed in the 1C_4 conformation, *i.e.* in a similar way as discussed for D-Man and D-Tal, then three OH-groups are on the

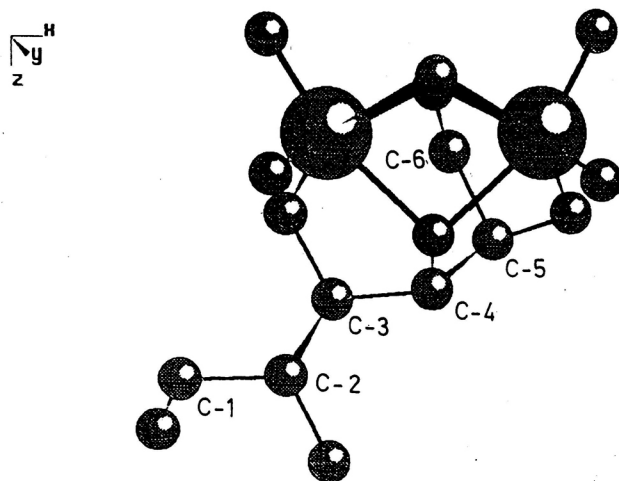
same ring side and can therefore give a stable complex (Scheme 1). This would explain the anomaly that a complex of (13) is formed although the otherwise essential C(2)-OH is lacking. No prediction of the signs is possible, however, since this is the only compound lacking the OH at C(2). Since we observed that 1,2-dideoxy-D-Gal (6) does not show any CD in the presence of molybdate, either three OH groups with *cis*-configuration or two *cis*-hydroxy groups and an *axially* arranged *cis*-CH₂OH group are obviously the minimal requirements for complexing. Moreover, from the series of chiral cyclic diols 1-4 and triols 5 and 6 all derived from aldopentose or aldohexoses, none gave observable CD effects on complexation with molybdate. There is another possible explanation of this phenomenon, however, based on the recent results of Bilik *et al.*⁸ They suggest the aldoses like 13 could be complexed in the acyclic form, using the *arabino* system including C(3)-C(6) hydroxy groups, which is absent in the polyols 1-6.*

The same geometry of binding is possible for D-Glc (9) and D-Xyl (15) and indeed their respective Cotton effects have all the same signs. With D-Man (10) and D-Tal (12), a similar type of binding is possible, but now with their ¹C₄ conformation, as their CD-curves are nearly enantiomorphous to those of the first mentioned sugars. L-Rham (17) could accommodate the necessary geometry only when the methyl C(6) is in axial conformation; in the other more stable chair form with equatorial methyl, the OH groups at C(1) to C(3) do not have the proper *a-e-a* conformation. If the latter is present, then the type of complexing would have to be different from all the others. It is indeed this compound that gives two Cotton effects,¹⁴ a positive one at 330 nm and a negative one at 296 nm, instead of the usual single one around 310 nm. Thus, such a CD indicates an equilibrium between two different species with opposite torsional angles of the O-C(2)-C(3)-O unit.

As it has been shown by the X-ray studies¹⁷ of the D-mannitol complex, the Mo₂O₇²⁻ is fully hydrated on both Mo atoms, so that actually an Mo₂O₉ unit (cluster) is present, with approximate octahedral geometry around each molybdenum. Three oxygens bridge the two metal atoms, two of which come from C(4) and C(6) of the D-mannitol unit. The oxygens at C(3) and C(5) are also involved in complexing, and in order to accommodate this, both octahedrons have to be distorted severely. The deviations from the colinear arrangement of the three O-Mo-O diagonals of the octahedron are 11°/11°, 26°/28°, and 41°/38°, respectively¹⁹ (Figure 4).

For the complex of the two hexitols, D-glucitol (7) and D-mannitol (8), we have found very similar CD-spectra as for most of the pyranoses (Figure 2.). This suggests that the configuration at C(2) is of no importance for the CD of these hexitols. Therefore, we can conclude that the structure in solution for both complexes is very similar to that found for the D-mannitol complex in the solid state,¹⁷ with the C(2)HOH-C(1)H₂OH moiety unbound, freely extended into solution. Such a binding is only possible in a stretched conformation but not for a cyclic structure, which must be present in the polyols 1-6 and pyranoses 9-17. The torsional angle around the bond C(1)-C(2) of a pyranose can adjust positively or negatively, whereas that of the O-C(2)-C(3)-O moiety is determined unequivocally by the configuration (and conformation) of the 6-membered ring. This is the torsional angle which governs the sign of the CD bands. In the open-chain hexitols, we have then to look from C(6) towards C(3), instead. The second and third torsional angles are both positive (+43°, +37°), and lead to a positive first and negative second Cotton effects.

* The authors are indebted to the referee who suggested this possible explanation of the CD phenomenon.



D-MANNITOL · Mo₂O₇

Figure 4. Solid state structure of the complex between dimolybdate and D-mannitol (computer graphics drawing according to ref. 17).

The results of our CD measurements for two hexytols require somewhat different interpretation from that set forth by Matulowa and Bilik,⁸ and Chapelle *et al.*,⁹ based on the ¹H-, ¹³C-, and ⁹⁵Mo-NMR data. The first group has found one complex of D-mannitol and three different complexes with D-glucitol, whereas the second group has found two complexes of D-mannitol (in 70:30 ratio), and even four complexes of D-glucitol (in 32:26:21:21 ratio). Such a discrepancy between the NMR and CD data may either be due to different techniques for preparing the complexes, or more probably, to the large difference of the concentration range used in the achiral spectroscopic methods and chiroptical methods, as indicated in the introductory paragraph in this section.

CD Spectra of the Complexes with Tungstate

Although polytungstates, along with polymolybdates, represent the most widespread class of polyoxoanions,²⁰ there are no reports either on the CD properties of their complexes with monosaccharides and polyols or on their possible catalytic activity in C(2) epimerization. First, it was interesting to find that only D-Man and D-Lyx, but not D-Glc and D-Xyl, gave a complex with APT, which CD spectra are shown in Figure 5. and 6.

This finding is in agreement with ¹³C- and ¹H-NMR data, that reported complexation of D-Man, D-Lyx, and some other aldose from the *lyxo*-series, but no complexation of D-Glc, D-Xyl, and some other aldoses from the *ribo*-series.⁶ Comparison with the CD of the AHM complex of 10 and 16, presented in Figures 5 and 6, reveals a strong hypsochromic shift (ca. 35–50 nm) of all CD bands of the tungstate complexes, along with ca. 20 times stronger Cotton effects. This parallels the finding that the aldoses from *lyxo*-series 12, 14 and 16, gave complexes with molybdate, log *K* 14.5, 15.0, and 13.9,

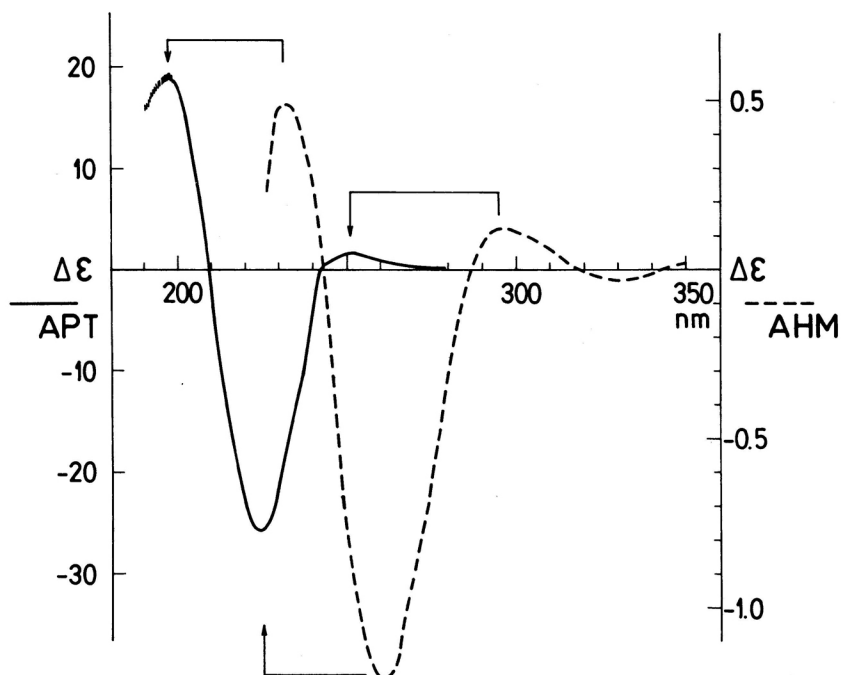


Figure 5. CD Spectra of tungstate complex of D-Man (10,—) and, for comparison, of the molybdate complex of the same monosaccharide (---).

respectively, which are by *ca.* 3 log *K* units less stable than their corresponding tungstate complexes, having log *K* 17.5, 18.1, and 17.0, respectively.⁷

Both hexitols, 7 and 8, also afford strongly CD active complexes with APT, Figure 7. As compared to the corresponding AHM complex (see Figure 3), all CD bands are regularly hypsochromically shifted by *ca.* 40–50 nm, and the Cotton effects at *ca.* 260–270 nm, and 210 nm, are *ca.* 5–10 times stronger. Again, these data can be compared with the stability constants, determined potentiometrically.²¹ The average log *K* values for molybdate and tungstate complexes with 7 are 8.0×10^{16} and 1.8×10^{19} , respectively, and with 8 are 7.8×10^{16} and 6.0×10^{18} , respectively. Thus, 8 forms slightly more stable complexes than 7, which is reflected in an almost double intensity of the CD bands of the tungstate complex of 8 as compared to 7, indicating much stronger conformational perturbations on binding of the former.

Whereas D-maltose (18) exhibited no CD in the presence of tungstate anion, it was interesting to observe that the APT complex of maltiol (19), an important sweetener available on hydrogenation of D-maltose (18), exhibited a nearly enantiomorphic CD curve as compared to the APT complex of D-glucitol (7), Figure 8. This could be explained by taking into account the facts that the D-Glc subunit in 19 does not complex

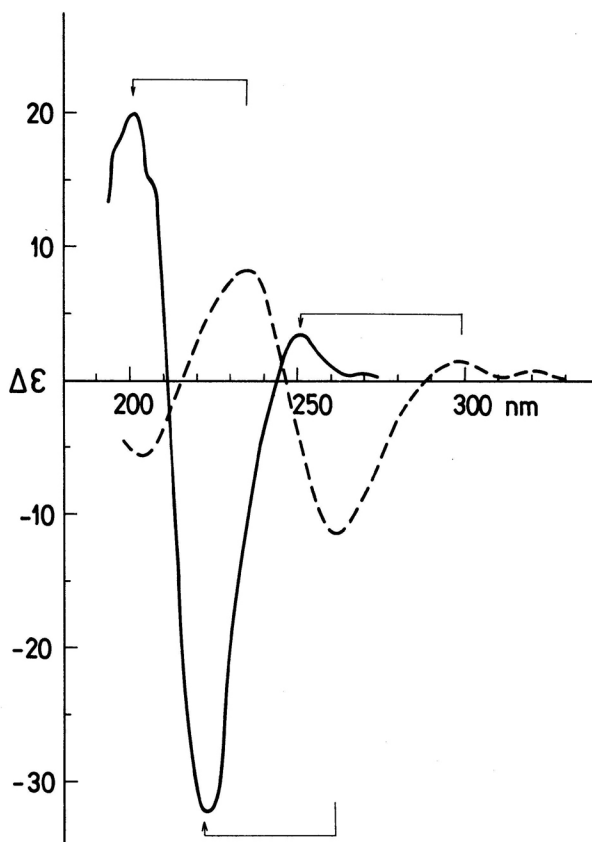


Figure 6. CD Spectra of tungstate (—) and molybdate (---) complex of D-Lyx (16).

with ATP, and that the binding region C(6)–C(3) in 19 is hindered by the glycosidic bond. There remain three vicinal OH groups, at C(1)–C(3), as the most probable binding site in 19. This region can adopt, in the complex, enantiomorphous conformation to that around C(3)–C(5) or C(4)–C(6) sequence in polyols 7 or 8, leading to the enantiomorphous CD curve.

CONCLUSIONS

a. CD Phenomena

In conclusion, we can state that this CD study of some oxo-(poly)molybdate-mono-saccharide and model-polyol complexes reveals an unequivocal correlation between the torsional angles around the 1,2,3-triol subunit of the complexed ligand and the Cotton effects between 325 and 300 nm, 280 and 260 nm, and that around 235 nm. Positive torsional angles in the case of 1,2-*cis*-2,3-*cis* triols lead to a positive first and second, and a negative third mentioned Cotton effect.

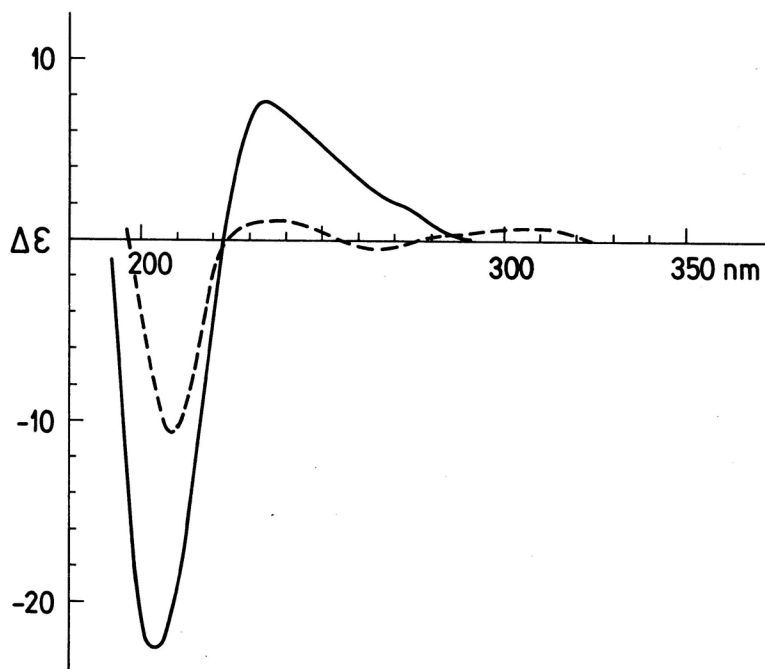


Figure 7. CD Spectra of tungstate complex of 7(—) and 8(---).

A positive first and a negative second torsional angle of this same triol moiety lead in general also to three such Cotton effects, but this time the first (small) Cotton effect at *ca.* 300 nm has the opposite sign to that between 280–260 nm, and can thus be easily recognized. If the bound C(OH) groups are not vicinal, then the *axially* disposed CH₂OH group becomes engaged in binding, forcing the pyranose ring into the energetically less favoured ¹C₄ conformation. In such cases two, or even more, conformers are bound. The open chain polyols 7 and 8 are bound through the sequence C(6)–C(5)–C(4)–C(3).

In the complexes with a ligand: Mo ratio of 1:2, the dimolybdate subunit must be highly distorted in order to enable a multicenter oxo-binding with one mole of the ligand. This is the actual chiral perturbation of d–d transitions of Mo(VI) that causes the observed Cotton effects. In the complexes of 1:1 type, two ligand molecules are bound per molybdate unit, which would render the whole oxo-complex less strained and lead to C₂ symmetry. Quite surprisingly, however, other spectroscopic data⁶⁻⁹ seem to exclude this type of dimolybdate-monosaccharide complexes.

Representatives of the monosaccharides from the *ribo*-series, D-Glc and D-Xyl, did not give any CD spectra in the presence of APT, whereas D-Man and D-Lyx, representatives of the *lyxo*-series, gave the CD bands which are *ca.* 5–10 times more intensive and by 30–50 nm hypsochromically shifted as compared to their AHM complexes. This indicates that the energy gap between the ground state and the excited state orbitals is significantly larger for APT – than for AHM complexes. Similar enhancement of in-

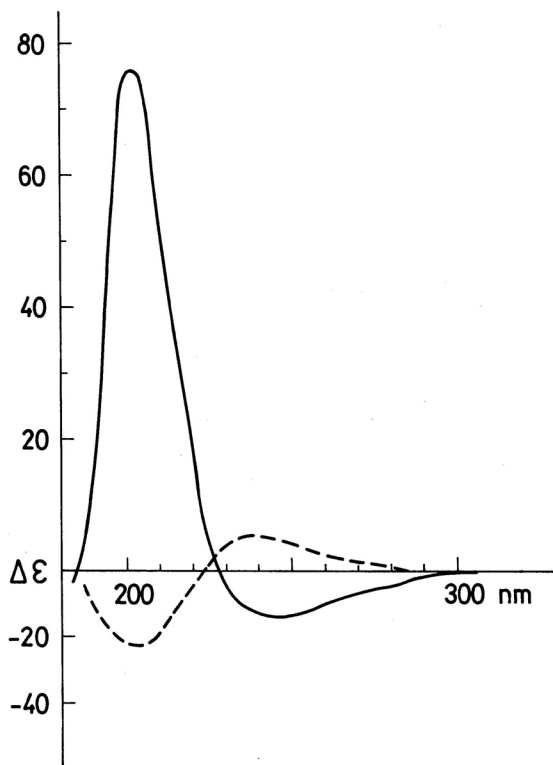


Figure 8. CD Spectra of tungstate complex of D-maltitol (19,—) and 7(---).

tensity and hypsochromic shifts were also observed for the APT complexes of the two hexitols 7 and 8. Interestingly, D-maltose (18) gave no CD in the presence of ATP, whereas its hydrogenation product D-maltiol (19) exhibited an almost enantiomorphic CD curve to the former hexitols, with very large Cotton effects, e.g. $\Delta\epsilon + 72$ at 203 nm. This relation can be explained by the different binding regions for 19, and for 7 and 8. The former polyol is presumably bound *via* the C(1)–C(3) sequence, which may adopt the conformation enantiotopic to that in the binding region of 7 and 8.

b: Catalytic Phenomena

The most surprising result, however, is the absence of any catalytic activity of APT in C(2) epimerization of the monosaccharides 9, 10, 16, and 17. All experiments were performed at the same catalyst-to-substrate ratio, and in the same temperature interval (70–90 °C) as for AHM.^{4,5} No satisfactory explanation of this phenomenon is possible until all detail about the catalytic epimerization mechanism is available. Some consistent conclusions, however, can be offered herein.

The crystal structures of HM and PT (polytungstate or dodecatungstate) anion are presented in Figure 9. In aqueous solution, however, PT seems to depolymerize into

the heptatungstate as the most stable species.²⁴ The most important difference between isopolymolibdates and isopolytungstates seems to reside in the smaller compressibility of the W^{+6} core than that of Mo^{+6} , and in the greater extension of the 5d vs. 4d orbitals. The first of these factors leads to less distorted WO_6 octahedra. The second factor implies that, at the observed M–O »single bond« distance of 1.92 Å in polyoxoanions, a better orbital d-sp³-σ-overlap is achieved with tungsten than with molybdenum. It is, therefore, argued that molybdates will tend to compensate for weak Mo–O single bonds by adopting structures that contain more multiple bonds than tungstates.²⁵

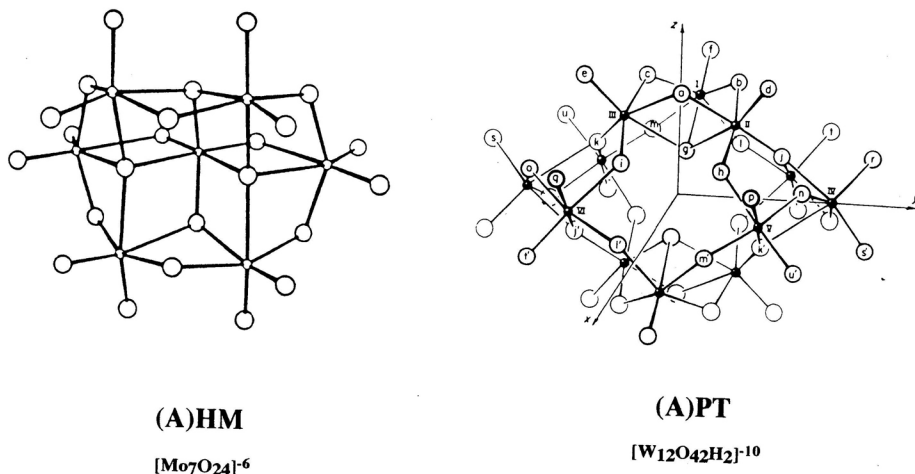
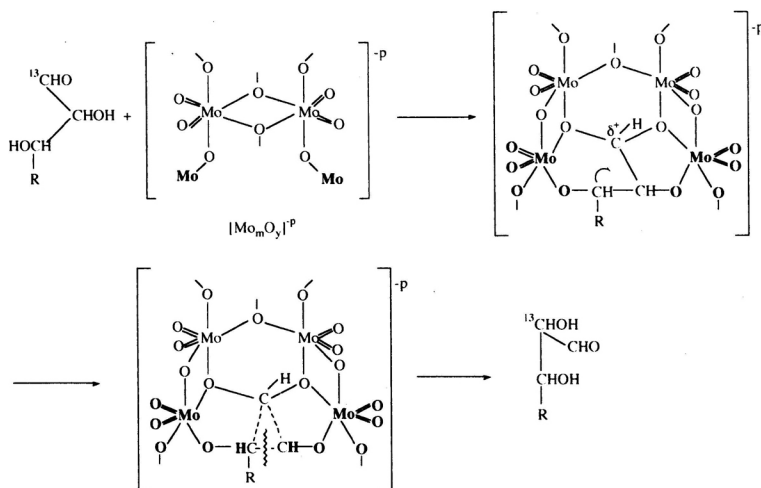


Figure 9. Crystal structures of HM anion (reproduced from ref. 22) and of PT anion (reproduced from ref. 23).

In view of the importance of such M–O_t (terminal) π-bonding in stabilizing polyoxoanion structures, it is necessary for both Mo^{+6} and W^{+6} to have vacant t_{2g} orbitals to accept the oxygen pπ electrons. This overlap seems to be more effective for Mo^{+6} than for W^{+6} , although there are no exact calculations.

On the other hand, it is known that reaction of molybdate anion with several aldehydes (not with ketones!) yields stable crystalline complexes of general formulae $[RCHMo_4O_{15}H]^{-3}$ ($R = CH_3, C_6H_5$).^{26,27} According to Day *et al.*,²⁶ one can consider these complex anions to be aldehyde adducts, the R–CHO binding site can be viewed as an acid-base pair site consisting of two coordinatively unsaturated molybdenum centers and a basic carbonyl oxygen. Consequently, it seems that dπ–pπ back donation in molybdate-aldehyde complexes stabilizes the partial positive charge on C(1) in the acetal-like subunit, maybe even better than in the carbonylic form of an aldehyde, favouring intramolecular nucleophilic attack at C(1) with concomitant skeletal rearrangement and inversion of configuration at C(2).³ Obviously, the difference in the delicate balance between metal-oxygen and carbon-oxygen bonding (bond strength and polarity) determines the appearance or absence of the catalytic activity in polyoxomolybdate and polyoxotungstate, respectively. The W–O distances for the exterior unshared

O atoms average 1.68 Å, while 2.38 Å is the average distance between W and the interior O *trans* atoms.^{28,29} The analogous distances in $[\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}]^{-3}$ complex amount to 1.80 Å (average), and 2.19 Å (for the H_2CO_2 subunit).²⁶ Thus, from the bond length alone, one cannot deduce the explanation for the absence of the catalytic activity in the former, and the presence in the latter.



SCHEME 2

The results described herewith point out the modified mechanistic model out of those put forward in our earlier papers.^{4,5} The interaction of $d\pi-p\pi$ can be envisaged, forming partially positive charge on C(1), Scheme 2, which undergoes formal nucleophilic attack by C(3), forming tridentric bond, as suggested by Barker *et al.*³ Stabilization of the charge in such an intermediate seems to be more effective in molybdate than in tungstate complex, making only the former an effective catalyst for C(2) epimerization.

Acknowledgement. – The authors are indebted to Dr. D. Horvatić, from IRB, for his help in searching crystallographic data, and for computer graphics of dimolybdate-D-mannitol complex, to Dr. G. B. Marin and Dr. A. Cibulsky from the University of Technology, Eindhoven, for informing us about their results prior to publication. This work was supported by the Joint Board for Scientific and Technological Cooperation between SFRJ and BR Deutschland (Jülich Programme).

EXPERIMENTAL

Compounds 1–4 are prepared as described in refs. 30, 31. Compounds 7–10, and 18, 19, as well as $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot x \text{H}_2\text{O}$, (*p.a.*, Aldrich), and $(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot \text{aq}$ (*puriss.* Fluka) were commercial samples, and were used without further purification.

1,2-Dideoxy-D-glucopyranose (5)

3,4,6-Tri-O-acetyl-glucal (1.79 g, 6.57 mmol), dissolved in ethylacetate (10 ml) and acetic acid (5 ml), was hydrogenated during 20 hours at 1.4 bar, in the presence of Pt/C (300 mg). The tri-

O-acetyl derivative of **5** was hydrolyzed for 1 hour with MeONa/MeOH (4.63 mmol in 10 ml) at ambient temperature, TLC control with CHCl₃/CH₃OH (9:1) as eluant. Crude **5** was purified on a silicagel column with CHCl₃-CH₃OH (85:15) affording the pure product, which crystallized while kept in the refrigerator, m.p. 86–87 °C (lit.³² m.p. 86 °C). IR_νmax.: 3400 (broad), 2970, 1380, 1080, 1020, 950, 910, 865, 815 cm⁻¹. ¹H-NMR (DMSO-d₆) δ in ppm: 4.44 (broad s, 3xOH), exchange with D₂O), 3.87–3.08 (m, 5H), 2.98–2.93 (m, 2H), 1.9–1.15 (m, C(2)–2H). ¹³C-NMR δ in ppm: 81.55 C(5), 72.29 C(3) and C(4), 64.84 C(1), 61.68 C(6), 34.26 C(2).

1,2-Dideoxy-D-galactopyranose (**6**)

Starting from 3,4,6-tri-O-acetyl-galactal (6.5 g, 23.2 mmol), **6** was obtained following the procedure as described for **5**. Pure **6** crystallized from ethanol-diisopropylether, m.p. 128–132 °C, lit.³³ m.p. 128 °C. IR: δ_{max}: 3380, 2980, 1465, 1435, 1185, 1150, 1070, 1010, 805, 760 cm⁻¹. ¹H-NMR (DMSO-d₆) δ in ppm: 4.40 (broad s, 3xH, exchangeable with D₂O), 3.95–3.40 (m, 5H), 3.3–3.15 (m, 2H), 2.0–1.5 (m, CV(2)–2H). ¹³C-NMR, δ in ppm: 79.69 C(5), 69.13, 67.89(C(3), C(4), 65.29C(1), 61.46, C(6), 209.29 C(2).

CD measurements were performed on a Dichrographe Mark III (ISA-Jobin-Yvon) connected on-line to a PC. Noise was eliminated by curve-smoothing according to the Golay/Savitzky³⁴ algorithm (best parabola of degree 3 fitted to 25 consecutive points). Characteristic data are collected in Table I.

TABLE I

CD Data for the AHM and APT Complexes of Compounds 7-11, 14, 16, and 19

Complex	CD [nm] (Δε)/in water
7 x AHM	325(+0.1), 274(+1.0), 239(-3.5), 209(+2.5)
7 x APT	260(+2.1), 233(+7.6), 204(-23)
8 x AHM	327(-0.1), 271(+1.5), 240(-6.0), 206(+4.9)
8 x APT	265(-0.3), 239(+0.7), 208(-11.0)
9 x AHM	340(+0.02), 279(+0.07), 240(-0.26)
10 x AHM	296(+0.14), 261(-1.3), 233(+0.51)
10 x APT	251(+2.0), 226(-25.2), 197(+19)
11 x AHM	340(+0.03), 278(+0.09), 242(-0.35)
15 x AHM	310(+0.2), 273(+0.8), 239(-2.5)
16 x AHM	320(+0.2), 297(+0.09), 261(-11.6), 235(+8.4), 206(-6.0)
16 x APT	250(+3.8), 226(-32.9), 202(-20)
19 x APT	275(-5.0), 241(-13.8), 203(+72)

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SAŽETAK

Heptamolibdatnim ionom katalizirana emiperizacija monosaharida. CD studija vezanja monosaharida i poliola na molibdat i tungstat

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CD-spektroskopijom proučena su konformacijska svojstva i slaba interakcija monosaharida u okso-kompleksima s amonij-heptamolibdatom (AHM) i amonij-paratungstatom (APT). Diskutira se o njihovu odnosu prema katalitičkoj C(2) epimerizaciji. Nađeno je za molibdatni kompleks da postoji jednoznačna korelacija između torzijskog kuta u 1,2,3-triolnoj podjedinici u vezanom monosaharidu i Cotton-ova efekta između 325 i 300 nm, 286 i 260 nm, i oko 235 nm. Pozitivni torzijski kut u 1,2-*cis*-2,3-*cis* triolima vodi do pozitivnog prvog i drugog, te negativnog trećeg Cotton-ova efekta. Predpostavljajući omjer 1:2 između monosaharida i iona Mo(VI) u kompleksu, što je indicirano nedavnom ⁹⁵Mo-NMR studijom, može se pretpostaviti vezanje monosaharida iz *lyxo*-serije u konformaciji ¹C₄, dok za *ribo*-seriju prevladava vezanje u konformaciji ⁴C₁. Prva skupina heksoza čini se da angažira C(6)H₂OH skupinu (ako je prisutna), dok se druga skupina veže preko 1,2,3-OH strukture u *cis*-konfiguraciji. Odsutnost CD efekta iz cikličkih poliola 1-6 dobivenih iz različitih piranoza, pokazuje da su minimalni strukturni zahtjevi za nastajanje CD-aktivnih okso-kompleksa ili tri OH skupine u *cis*-konfiguraciji, ili dvije *cis*-hidroksi-skupine i jedna aksijalno smještena *cis*-CH₂OH skupina. Dva heksitola, D-glucitol 7, i D-manitol 8, daju također 1:2 komplekse, angažirajući četiri hidroksi-skupine »od kraja« lanca C(6)-C(3), kao što je nađeno

analizom X-zrakama za kristalni kompleks D-manitola. Taj način vezanja ostavlja nevezan C(2), jedini kiralni centar sa suprotnom konfiguracijom u ta dva liganda, dajući vrlo slične spektre CD za oba kompleksa.

S amonijevim paratungstatom (APT) D-Man (10) i D-Lyx (16), ali ne i D-Glu (9) i D-Xyl (15), daju CD aktivne komplekse, čiji su svi Cotton-ovi efekti *ca.* 5-10 puta intenzivniji i hipsokromno pomaknuti (za *ca.* 30-40 nm) s obzirom na njihove AHM komplekse. Slično povećanje intenziteta i hipsokromni pomak opaženi su za APT komplekse dva heksitola 7 i 8. Dok APT s disaharidom D-maltozom (18) ne daje CD, D-maltitol (19) daje gotovo enantiomorfnu CD-krivulju u odnosu na dva spomenuta heksitola, ali s vrlo jakim Cotton-ovim efektima, na pr. $\Delta\epsilon + 72$ kod 203 nm. Ovaj odnos CD-krivulja može se objasniti različitim regijama u kojima se vežu 7 i 8 u odnosu na 19. Posljednji spoj vjerojatno je vezan preko sekvencije C(1)-C(3), koja može poprimiti konformaciju enantiotopnu za onu u veznom području spojeva 7 i 8.

Posebno pak iznanađuje potpuna odsutnost katalitičkog efekta APT na C(2) epimerizaciju D-Glc, D-Man, D-Xyl, i D-Lyx. Ovo se može objasniti različitim stupnjem M--O $d\pi-p\pi$ interakcije u dva izopolianiona. Čini se da tungstat-anion slabije stabilizira putem povratnog davanja elektrona parcijalni pozitivni naboj na C(1) u kompleksiranim aldozama, što se čini nužnim za pregradnju koja vodi do C(2) epimerizacije.