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COMPLEXES BETWEEN POLYHYDROXY-COMPOUNDS AND INORGANIC OXY-ACIDS.

TUNGSTATE COMPLEXES OF SUGARS AND OTHER CYCLIC POLYHYDROXY-COMPOUNDS

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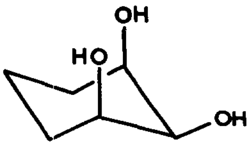
In previous papers[1,2] we have shown that molybdate, in common with ions of other inorganic oxy-acids[3], forms ionic complexes with certain polyhydroxy-compounds. It was already known that tungstate enhances the specific rotation of D-mannitol[4]. The use of tungstate complexes in paper electrophoresis was briefly studied by Frahn and Mills[5]. The present investigation, in which tungstate was used as the inorganic oxy-acid ion, was of interest because of the close resemblance between the chemistry of molybdenum^{VI} and that of tungsten^{VI}, particularly with respect to their oxygen compounds.

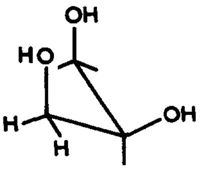
The specific rotations of D-mannose and D-ribose in tungstate solutions of pH 6.0 and pH 6.7, respectively, where maximal changes occur, are affected by the relative concentration of the two components. The results are typical of an equilibrium reaction. Measurements with continuous variation of concentration of both components have shown that the complexes formed from D-mannose and D-ribose contain the tungsten atom and the monosaccharide in the ratio 1:1. It is reasonable to assume that complexes formed from the compounds discussed below and which contain the same essential structural features as D-mannose and D-ribose are of the same type.

An examination was made of the behaviour of sugars and other cyclic polyhydroxy-compounds during paper electrophoresis in tungstate solution of pH 5. D-Glucitol was used as a standard for comparison of rates of migration, and glycerol or hydroxymethylfurfural as a non-migrating marker for correction of electro-osmosis. Migration rates are thus expressed as M_S(*W*) or M_S(*Mo*) values. *W* and *Mo* refer to the electrolytes tungstate and molybdate, respectively.

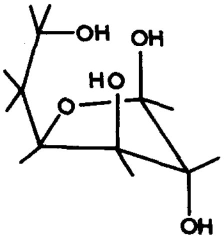
Previously, we established that sugars and other six-membered cyclic polyhydroxy-compounds complex significantly with molybdate only if they possess a *cis*-*cis*-1,2,3-triol system and thus, in one of their chair conformations, one equatorial hydroxyl group neighboured by two axial hydroxyl groups [1(*ax*),2(*eq*),3(*ax*)-triol system, (I)].[1] Alternatively, complexing with molybdate occurred when three hydroxyl groups could assume an equivalent spatial disposition, e.g. when one of the hydroxyl groups was not attached to a ring carbon atom (II). The present results show that the same type of "tridentate" complexes are formed with tungstate.



I



II



III

M_S Values of polyhydroxy-compounds

Migrating compounds

	$M_S(W)$	$M_S(Mo)$
D-Erythrose	0.2 - 1.1	0.9[1]
L-Threose	0.05	0.6[1]
D-Lyxose	0 - 1.0	1.1[1]
D-Ribose	0.2	0.4[1]
D-Gulose	1.1	1.1[1]
6-Deoxy-D-gulose	1.1	1.1
D-Mannose	0 - 1.1	0 - 0.9[1]
6-Deoxy-L-mannose	0 - 1.1	0 - 0.6[1]
5-Deoxy-D-*xylo*-hexose	0.3	0.7
Alloinositol	0.1	0.4[1]
Epi-inositol	1.0	1.1[1]

Non-migrating compounds $M_S(W) < 0.05$

Glyceraldehyde
L-Arabinose
Methyl α-D-lyxopyranoside
Methyl α-D-ribopyranoside
D-xylose
2-Deoxy-D-*erythro*-pentose
D-Galactose
6-Deoxy-D-galactose
D-Glucose
3-O-Methyl-D-glucose
4-O-Methyl-D-glucose
6-O-Methyl-D-glucose
6-Deoxy-D-glucose
Methyl α-D-glucopyranoside
3,4-Di-O-methyl-D-mannose
Methyl α-D-mannopyranoside
2-Deoxy-D-*arabino*-hexose
2-Deoxy-D-*lyxo*-hexose
2-Deoxy-D-*ribo*-hexose
2-Deoxy-D-*xylo*-hexose
(+) - Inositol
Mucoinositol
Myoinositol
Scylloinositol

Cyclitols.- The rates of migration of cyclitols during electrophoresis in molybdate solution have been related to the instability factors of the conformations which have the 1(ax),2(eq),3(ax)-triol system (I).[1] This influence of instability factors is more pronounced in the case of tungstate.

Aldoses.- The overall pattern of electrophoretic mobilities of aldopentoses and -hexoses in tungstate solution is similar to that in molybdate solution, although the enhanced effect of instability factors described above was again observed (cf. D-ribose and methyl α-D-ribo-pyranoside in molybdate and tungstate). Substitution in, or replacement of, at least one of the hydroxyl groups of the cis-cis-1,2,3-triol system destroys the ability to form a complex with tungstate. On the other hand, substitution in or of hydroxyl groups other than those of the cis-cis-1,2,3-triol system has no effect on complex-formation.

5-Deoxy-D-xylo-hexose is so far the only monosubstituted derivative of D-glucose (or L-idose) which has been shown to complex with tungstate or molybdate. It could complex in its aldehydo form since the spatial disposition of the hydroxyl groups on $C_{(2)}$,$C_{(3)}$, and $C_{(4)}$ of the planar zig-zag conformation is identical with that in (I). The same should apply for D-glucose which, however, shows no tendency to adopt this form. On the other hand, evidence is now accumulating that one of the ring atoms of five-membered ring systems is out of plane[6,7]. The result is that atoms attached to adjacent ring-atoms become slightly staggered. Similarly, $C_{(2)}$ of 5-deoxy-D-xylo-hexofuranose could be out of plane. The hydroxyl groups on $C_{(1)}$,$C_{(3)}$, and $C_{(6)}$ of its β-anomer could then be brought into the same spatial disposition (III) as those of (I). Thus, electrophoresis in tungstate (or molybdate) solution can be regarded as a method to distinguish between the aldehydo, furanose and pyranose forms of D-glucose; it might well be applied in the future to other appropriate sugars.

Both the aldotetroses, erythrose and threose, migrate during electrophoresis in tungstate (and molybdate) solution. The argument applied to 5-deoxy-D-*xylo*-hexose can be extended to both compounds. D-Erythrose possesses three hydroxyl groups in a spatial disposition approximating to that of (I) only in its α-furanose form, whereas the hydroxyl groups of the aldehydo form only of L-threose can be brought, without distortion of bond angles, into this arrangement.

2-Amino-2,6-dideoxy-D-*talo*-hexose (hydrochloride) migrated during electrophoresis in tungstate and molybdate solutions (pH 5) towards the cathode and at approximately the same rate as 2-amino-2-deoxy-D-*gluco*-hexose hydrochloride. In tungstate solution (pH 7.7) 2-amino-2,6-dideoxy-D-*talo*-hexose migrated towards the anode with a mobility of *ca.* $6 - 12 \times 10^{-5}$ cm.^{2} V^{-1} sec.$^{-1}$, whereas 2-amino-2-deoxy-D-*gluco*-hexose remained immobile. This indicates that at least one hydroxyl group of the triol system (I) can be replaced by a primary amino group.

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