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Note

Sugar complexes of Sn(IV), Sb(V), and Te(VI) hydroxyanions

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The reactions of carbohydrates and other polyhydroxy compounds with certain weak inorganic oxyacids and oxyacid anions have been the subject of several publications[1–4]. With telluric acid, the formation of mainly 1:1 chelates was claimed[2,5], although little attention was paid to higher pH values where significant results have recently been obtained[6–8]. The investigation has been extended[8] to the isostructural and isoelectronic hexahydroxyanions of Sn(IV) and Sb(V), since relatively little is known about their chelates with higher polyols[1,9], and this aspect is now further reported.

The conductance and pH of an alkaline solution of telluric acid decrease when a suitable sugar is added. This effect is accompanied by a decrease in equilibration time, which reduces from ~24 h at pH 4.8 to within 15 min at pH 11. Upon plotting[10] the measurements against the tellurate–polyol molar ratio, the presence of solely 1:1 complexes at low pH was confirmed with D-erythrose, L-threose, D-ribose, L-arabinose, D-xylose, D-lyxose, D-glucose, D-gulose, D-altrose, D-allose, D-galactose, D-mannose, D-talose, D-idose, L-rhamnose, D-fructose, L-sorbose, and D-tagatose. With the exception of the aldotetroses, complexes of higher tellurate–polyol composition were indicated at alkaline pH. Thus, at pH 11, in addition to the expected 1:1 complexes, 1:2 polyol–tellurate chelates were observed with each of the above aldopentoses, aldohexoses, and ketoses. Evidence for 1:3 complexes was obtained with maltose, lactose, cellobiose, and sophorose, whereas sucrose[6], nigerose, melibiose, gentiobiose, isomaltose, and trehalose formed 1:4 complexes. Raffinose and melezitose formed 1:2 and 1:5 chelates (Fig. 1). In the pH range 8–10, evidence for complexes of intermediate stoichiometries were obtained with some of these oligosaccharides (*cf.* Fig. 1).

The above data were consistent with those obtained by polarimetry. The $[\alpha]_D$ values of D-fructose, sucrose[6], lactose, and galactose were enhanced in the presence of telluric acid, progressively with increase in pH. With maltose and L-arabinose (Fig. 2*a*), chelation diminished the $[\alpha]_D$ value. Similar investigations also confirmed the existence of a chelate of the type raffinose–(tellurate)$_5$ at pH >10 (Fig. 2*b*),

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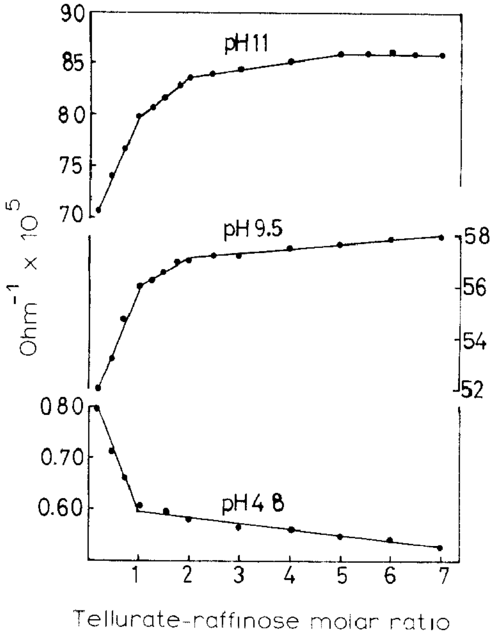

Fig. 1. Effect of the addition of raffinose on the conductance of 0.01M telluric acid at various initial pH values and at 25°.

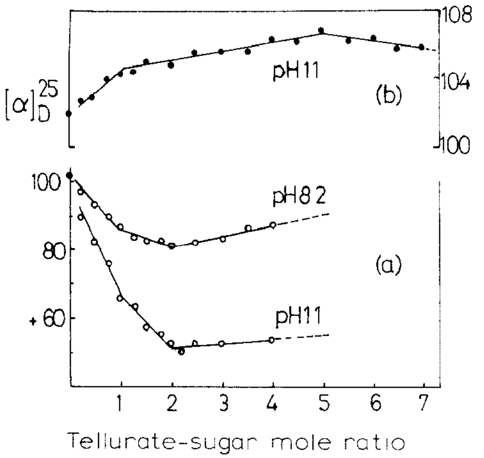

Fig. 2. Specific optical rotations of (*a*) L-arabinose and (*b*) raffinose pentahydrate in 0.05M tellurate.

leaving little doubt as to the presence of some 1:3 and 1:4 complexes, most likely as transient species, provided that tellurate was present in sufficiently large excess.

Progressive addition of sugars to 0.01M potassium antimonate, initially at its natural pH (7.45), was accompanied by a gradual decrease in conductance, with little change in pH. The Yoe–Jones[10] conductance plots indicated the exclusive formation of 1:1 complexes. In more alkaline solution, both the conductance and the pH were lowered in a fashion which confirmed that 1:1 complexes were still the main species present even at higher concentrations of antimonate. In only two instances was a mixture of 1:1 and 1:2 polyol–oxyanion complexes indicated, namely, with raffinose and melezitose, at initial pH 12. The $[\alpha]_D$ values of maltose and raffinose were lowered in the presence of antimonate and an increase was observed for D-glucose. Plots of $[\alpha]_D$ against the antimonate–polyol molar ratio ascertained the formation of 1:1 sugar–antimonates. In contrast to hexitols[8], the addition of D-glucose to acidified potassium antimonate initially at pH 4 *raised,* rather than lowered, the pH of the solution. The same effect was also observed with sucrose, raffinose, and most of the other sugars investigated. This behaviour is evidence for the relatively poor ability of antimonic acid to bind simple and higher sugars.

The interaction of hexahydroxystannate anions with carbohydrates in aqueous media is similar to that of antimonate. At its natural (11.7, 0.01M) and higher pH (up to 12.7), conductimetric and pH measurements on sodium stannate showed a decrease when carbohydrates were added. A plot of these data gave discontinuities at 1:1 stannate–sugar molar ratios indicative of 1:1 chelates. This effect was observed with each of the compounds studied and there was no unambiguous evidence for the presence of other complexes. The use of polarimetry to supplement and/or confirm these results was hampered by the turbidity of the solutions. Equilibration times for both antimonate– and stannate–polyol systems were usually within 3 days at 25°, the longest times being observed at the highest pH values so that the possibility of acid-catalysis cannot be discounted.

Polyol–oxyanion chelate formation is generally accepted[5] as involving two hydroxyl groups of the oxyanion and two suitable hydroxyl groups from the polyol. Apparently, vicinal *cis* and *trans* hydroxyl groups in pyranoses complex readily with tellurate ions. It is plausible[5] to assume that only when these hydroxyl groups have been complexed do any remaining 1,3-hydroxyl groups on the molecule become involved, with high pH providing a stabilising effect. For raffinose [*O*-α-D-galactopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→2)-β-D-fructofuranoside], for example, a 1:5 chelate can be afforded by complexation at HO-2,3 and HO-4,6 of the galactopyranosyl group, HO-2,3 or HO-3,4 of the glucopyranosyl residue, and HO-1,3 and HO-4,6 of the fructofuranoside residue. Similar structural considerations readily reveal why only up to 1:3 tellurate complexes are formed with maltose, lactose, cellobiose, and sophorose, whereas 1:4 complexes are possible with sucrose, nigerose, melibiose, gentiobiose, isomaltose, and trehalose, although each possesses eight hydroxyl groups. It is thought that few such chelates are formed with antimonate or stannate since their ionic size is larger than that of tellurate[8].

The foregoing results suggest as a general rule that, whereas antimonate and stannate form mainly 1:1 complexes with polyols, tellurium-richer chelates are possible only in alkaline media.

EXPERIMENTAL

The conductimetric, polarimetric, and pH measurements on solutions containing various oxyanion–polyol molar ratios have been described[6–8]. Optical rotations at 25° (4-dm path-length) were measured at 589 nm with a Hilger spectropolarimeter. Only those sugars with a sufficiently large specific rotation were studied.

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