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SUGAR COMPLEXES WITH CALCIUM ION: INFRARED SPECTRA OF CRYSTALLINE D-GLUCURONIC ACID AND ITS CALCIUM COMPLEXES

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ABSTRACT

The Fourier-transform infrared spectra of D-glucuronic acid and three of its Ca^{2+} complexes have been recorded. These complexes are of the type Ca(D-glucuronate)X · $3H_2O$ and Ca(D-glucuronate)$_2$ · $4H_2O$, where X = Cl^- or Br^-. The structurally identified Ca(D-glucuronate)Br · $3H_2O$ shows that the octacoordination of each Ca^{2+} ion is completed by three D-glucuronate residues and two water molecules. The D-glucuronate anion binds calcium cations through three chelation sites: one that involves a carboxyl–oxygen atom combined with O-5; one that includes the second carboxyl–oxygen atom acting in concert with O-4; and one involving the O-1–O-2 pair of hydroxyl groups. Spectroscopic evidence shows that the calcium halide complexes of D-glucuronic acid are structurally related in terms of 8-coordination and the common coordination-sites involved, whereas Ca(D-glucuronate)$_2$ · $4H_2O$ shows 8-coordination but in different structural arrangements. The strong, intermolecular hydrogen-bonding network of the free sugar is preserved upon metalation, whereas the intramolecular hydrogen-bonding system breaks down upon acid ionization. It is also evident that the D-glucuronate crystallizes as the α anomer in this series of metal complexes.

INTRODUCTION

Calcium ions and sugars appear to participate in a variety of biological adhesion and agglutination processes, particularly those occurring at cell surfaces[1]. Calcium ions show great affinity for complexation with polysaccharides, and structural studies of Ca–sugar complexes have been the subject of many recent reports[2]. Although the i.r. spectra of sugars have been studied in detail[3,4], structural information on metal–sugar complexes has been limited to data from X-ray crystallographic[2] and proton or carbon-13 n.m.r.-spectral analysis[5,6].

In the present paper, the F.t.-i.r. spectra of D-glucuronic acid and its calcium complexes are examined for the first time. The spectroscopic properties of all Ca–glucuronate complexes synthesized in this laboratory are compared with the i.r. spectra of the structurally characterized[7] Ca(glucuronate)Br · $3H_2O$. This has permitted observation of characteristic features and the establishment of a correlation

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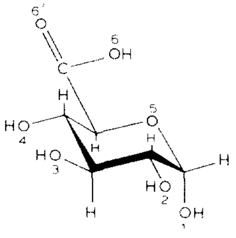
between the spectral changes and the coordination sites, used by the sugar, in each structural type of calcium-complex.



This discussion is largely based on the assignments and the normal-coordinate analysis reported by Hineno[3] and Vasko *et al.*[4], and is in good agreement with their observations.

EXPERIMENTAL

D-Glucuronic acid was BDH reagent-grade and was recrystallized from water.

Preparation of calcium-complexes. — Calcium halide complexes were prepared as reported[7] and were crystallized from water by slow evaporation. Ca(D-glucuronate)$_2$ · $4H_2O$ was prepared by adding 2 mmol of the acid in water (20 mL) to 1 mmol of calcium carbonate suspended in water (20 mL). The solution was decolorized with activated charcoal and crystals of the calcium salt were formed by slow evaporation. The compounds were hygroscopic, soluble in water, and slightly soluble in hot alcohol, but were not soluble in any other common organic solvents.

The F.t.-i.r. spectra were recorded with potassium bromide pellets and a DIGI-LAB FTS-15/C Fourier-Transform Michelson i.r. interferometer, equipped with a high-sensitivity HgCdTe detector and a KBr beam-splitter, having a spectral resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

The i.r. spectra of free D-glucuronic acid and its metal complexes were recorded in the region of 4000–400 cm^{-1}, and they are discussed separately, (*a*) 4000–2700 cm^{-1} and (*b*) 1800–400 cm^{-1}.

(a) *4000–2700 cm*$^{-1}$. — In this region, the free sugar shows four strong and broad absorption bands centered at ~3400, 3280, 3160, and 2900 cm^{-1} (Fig. 1). The first three absorption bands are related to the hydrogen-bonded OH stretching vibrations[3,4] and the last one is assigned to the C–H stretching vibrational frequencies[3,4] (Table I). The absorption bands at 3400 and 3280 cm^{-1} arise from the strong, intermolecular hydrogen-bonding network[8] of the free acid, whereas the absorption band at 3160 cm^{-1} may be attributed to the intramolecular hydrogen-

TABLE I

FOURIER-TRANSFORM INFRARED ABSORPTION BANDS (CM^{-1}) OF CRYSTALLINE D-GLUCURONIC ACID AND ITS CALCIUM COMPLEXES

D-*Glucuronic acid*	*Ca(glucuronate)$_2$ · 4H$_2$O*	*Ca(*D-*glucuronate)Cl · 3H$_2$O*	*Ca(*D-*glucuronate)Br · 3H$_2$O*	*Possible assignment*[a]
3450 sh	3470 m	3480 m	3490 m	νOH(hydrogen) bonded)[3,4,11]
3400 b	3370 b	3365 s	3375 s	
		3356 s	3360 s	
3290 sh	3280 m	3285 sh	3290 sh	
3280 s	3260 s	3255 vs	3265 vs	
3160 b				
2926 m	2925 w	2930 w	2940 w	νCH[3,4,11]
2887 s	2890 w	2900 vw	2895 vw	
2840 m	2840 w	2850 vw	2845 vw	
2766 w		2760 vw		overtone
1707 vs				νC=O[11]
		1664 s	1663 s	δH_2O[13]
	1604 bs	1615 sh	1604 sh	νC=O antisymmetric[13]
	1600 sh	1600 bs	1597 vs	
1489 sh	1413 bs	1450 sh	1434 s	νC=O symmetric[13]
1457 s		1396 s	1390 m	δ(OCH) +δ(CCH)[3,4]
1363 sh	1375 m	1350 m	1348 w	δ(CCH) +δ(COH)[3,4]
1345 s		1335 m	1335 w	δ(CCH) +δ(COH)[3]
1325 s		1310 w	1300 w	δ(CCH) +δ(COH) +δ(OCH)[3]
1300 sh	1300 m	1271 m	1290 vw	
1259 s		1253 w	1250 w	δ(CCH) +δ(COH)[3]
1227 s	1223 w	1225 w	1220 w	δ(COH) +δ(CCH)[3]
1205 m				
1159 s	1157 m	1149 s	1145 s	ν(CO) +ν(CC) +δ(CCC)[3]
1140 s	1109 m	1103 s	1099 m	ν(CO) +ν(CC) +δ(CCO)[3]
1100 sh	1105 s	1078 m	1072 sh	
1089 vs		1062 s	1060 s	ν(CC) +ν(CO)[3]
1046 sh	1043 bs	1033 vs	1035 vs	ν(CO) +δ(CCO) +δ(CC)[3]
1024 vs	1000 sh	1014 s	1016 m	
960 sh	950 sh	957 s	955 m	ν(CO) +δ(CCH)[3]
944 m		905 m	910 m	
900 vw	900 w			ν(CC) +δ(CCH) +δ(CO)[3]
	807 m	821 s	816 s	δ(CH) of α-anomer[4]
770 m		792 w	790 vw	τ(CO) +δ(CCO) +δ(CCH)[3]
740 m	753 m	766 m	761 w	
715 s		713 w	702 m	(CCO) +(OCO) +τ(CO)[3]
690 m	690 vw	692 m	680 vw	δ(CCO) +τ(CCO)[3]
	670 w	663 w	669 vvw	
600 w	606 m	636 s	635 s	τ(CO)[3]
580 m		577 s	573 m	
570 m		557 vw	557 w	τ(CO) +δ(CCO)[3]
560 m		543 vw	545 vw	
530 m	530 m	520 s	520 m	
480 w		478 s	482 m	δ(CCO) +ν(CO)[3]
460 m				
450 m	450 w			
430 w		434 w	445 w	δ(CCO) +δ(CCH)[3]
420 m		422 m	420 w	
	420 m		405 w	

[a] s, strong; v, very; sh, shoulder; b, broad; w, weak; m, medium; δ, stretching; ν, bending; τ, internal rotation.

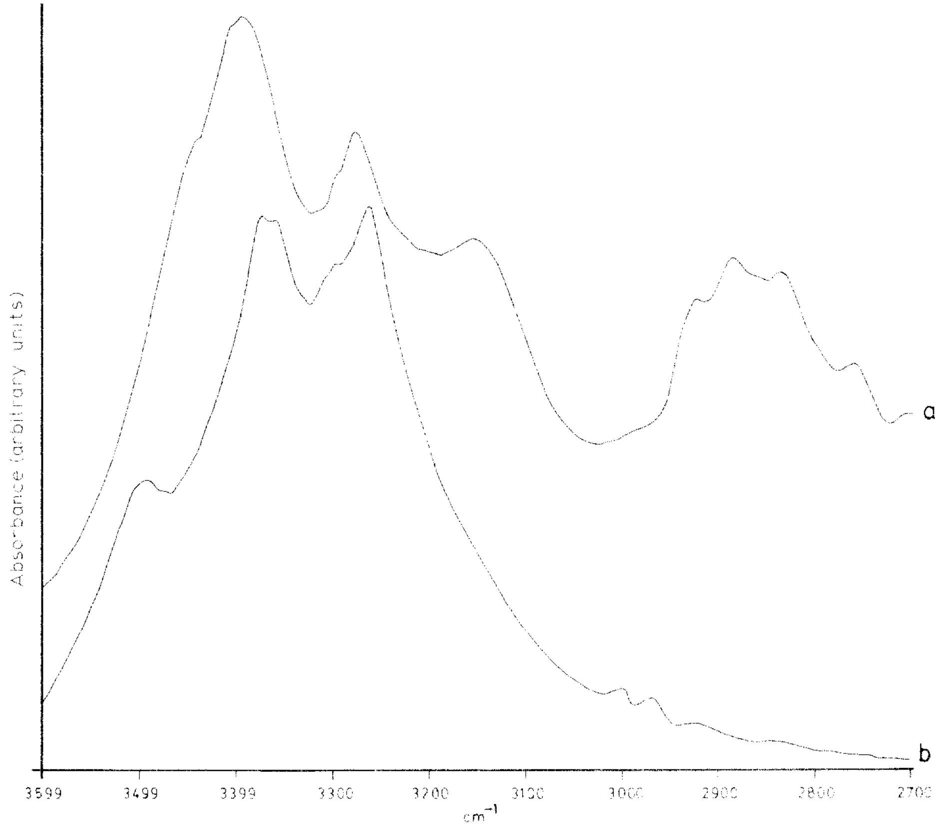


Fig. 1. Fourier-transform infrared spectra of D-glucuronic acid and its salts in the region 3600–2700 cm^{-1} for: (*a*) D-glucuronic acid; and (*b*) Ca(D-glucuronate)Br · 3H_2O.

bonding system[9] of the free sugar, which causes lowering and broadening of the OH stretching frequencies[10]. The absorption bands arising from the intermolecular hydrogen-bonding of the free sugar shift to a lower frequency ($\Delta\nu$ 25 cm^{-1}) upon metalation, and the absorption band at 3160 cm^{-1} disappears upon ionization of the acid (Table I and Fig. 1). The changes observed indicate that metalation of the free sugar breaks the intramolecular hydrogen-bonding system of the free sugar, whereas the strong, intermolecular hydrogen-bonding network is retained upon metal complexation[7]. The intramolecular hydrogen-bonding system is caused by the presence of the carboxylic group[11] in this sugar, as such a broad absorption-band (3160 cm^{-1}) does not appear in the spectra of α-L-arabinose and its metal complexes[12]. An absorption band of moderate intensity at 3450 cm^{-1} in the spectra of the free sugar, related to a weakly hydrogen-bonded OH group[12], shifts to higher frequency (3490 cm^{-1}) in the spectra of the calcium–sugar complexes. The C–H stretching vibrations of the free ligand at 3000–2800 cm^{-1} appeared, as weak absorption bands, in the same region in the spectra of the metal complexes. The

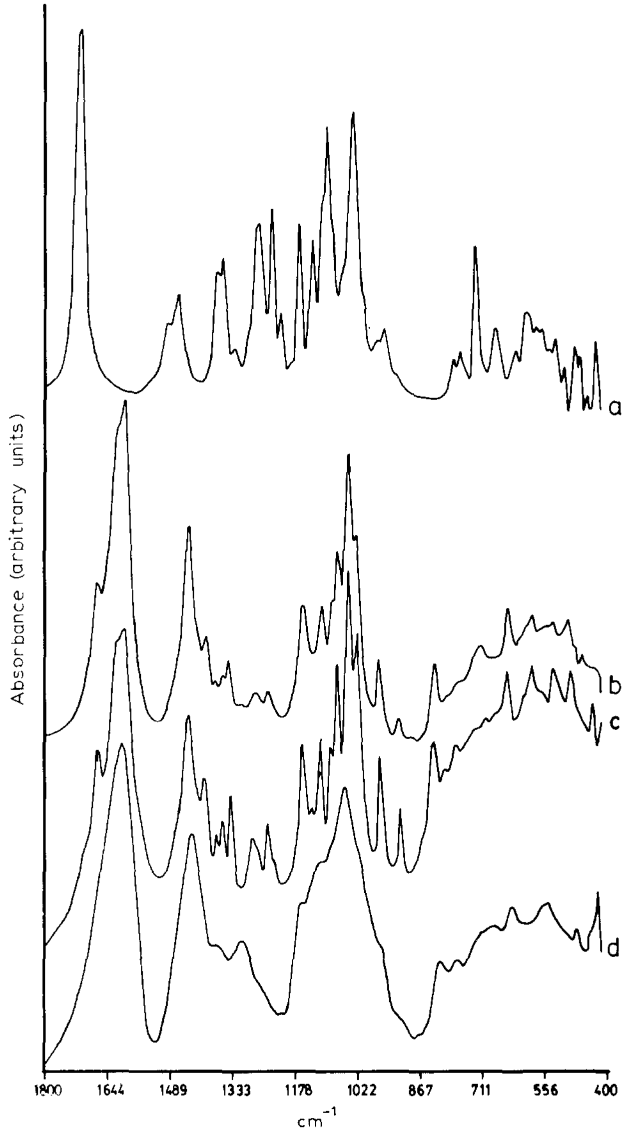


Fig. 2. Fourier-transform infrared spectra of D-glucuronic acid and its salts in the region 1800–400 cm^{-1} for: (*a*) D-glucuronic acid; (*b*) Ca(D-glucuronate)Br · $3H_2O$; (*c*) Ca(D-glucuronate)Cl · $3H_2O$; and (*d*) Ca(D-glucuronate)$_2$ · $4H_2O$.

main features of the spectra relevant to this discussion, together with the possible assignments, are given in Table I and Fig. 1.

(b) *1800–400 cm^{-1}*. — A strong absorption band at 1707 cm^{-1} of the free acid, related to the C=O stretching vibration[12], shifts to lower frequency and splits into two strong absorption bands, at ~1600 and 1450 cm^{-1}, in the spectra of the calcium complexes (Fig. 2). These two absorption bands are assigned to CO_2^- antisymmetric and symmetric stretching-vibrations[13], respectively. The splitting and shifting of the C–O stretching vibration of the sugar upon complexation is indicative of participation of the carboxylic oxygen atoms (O-6–O-6′) in metal–sugar bonding[7]. The extent of CO_2^- splitting, and the symmetric and antisymmetric stretching-frequencies (separation 150 cm^{-1}), indicated chelation or bridging[13] of the acid anions in these metal–sugar complexes[7].

The bending vibration of the coordinated water molecule[13] appeared as a shoulder absorption-band at 1650 cm^{-1} in the spectra of the metal complexes, except for that of $Ca(D\text{-glucuronate})_2 \cdot 4H_2O$, where it was obscured by the strong and broad carbonyl absorption. The strong absorption of the bonded water molecule, at ~3500 cm^{-1}, was overlapped by the strong hydrogen-bonding system of the glucuronate residue in these sugar complexes (Figs. 1 and 2).

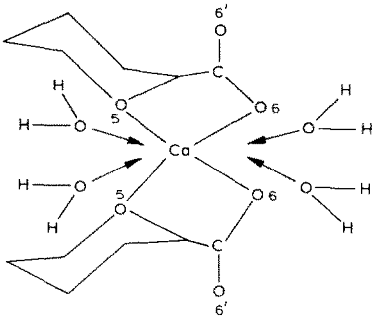
Ring CO and O–H bonding modes. — In this region, drastic changes occurred in the spectra of the sugar upon metalation. The atomic motions of the sugar ring-system are strongly coupled and the vibrational frequencies are spread over the entire molecule, and therefore individual assignments for each absorption band are difficult to make. However, the most common and meaningful changes observed are summarized here.

Seven absorption bands of strong and moderate intensities, appearing at 1365–1205 cm^{-1} in the spectra of the free acid and assigned mainly to the bending motions of CCH and COH[3,4], decreased in intensity and shifted to lower frequency in the spectra of the calcium–sugar complexes (Table I). This shift of the COH bending vibration to lower frequency is caused by participation of the OH group in metal–sugar bonding. The three strong absorption bands at 1159–1024 cm^{-1} in the spectra of the ligand, assigned to CO stretching frequencies[3], appeared in the i.r. spectra of the metal complexes (Table I) as one strong absorption band at 1035 cm^{-1} and as shoulder bands for the other absorptions at lower frequencies. The lowering of CO frequencies ($\Delta\nu$ 25 cm^{-1}) showed complexation of the ligand through the CO oxygen atoms of the glucuronate residues.

It has been found by Bugg *et al.*[7] that the D-glucuronae ion crystallizes as the α anomer in these calcium complexes, whereas the β anomer preponderates in aqueous solution and in the crystal structures of potassium and rubidium glucuronates[14]. It has also been suggested that the calcium ions have different affinities for the β and α anomers of certain sugars in aqueous solution[15], and thus it is possible that the calcium interaction influences which anomeric form of the D-glucuronate anion is favored. In the spectra of the calcium complexes, a sharp absorption-band appeared at 815 ±5 cm^{-1} (absent in the spectra of the free acid and its Na^+, K^+, and Rb^+ salts[12]). This is consistent with the presence of the D-glucuronate residue as the α anomer[4,16] in these sugar complexes.

Because of the presence of many ligand absorption-bands at 800–600 cm^{-1}, it was not possible to relate any absorption band to the wagging and rocking motions (800–700 cm^{-1}) of the coordinated water molecules in this region[13].

Ca(D-*glucuronate*)$_2$ · $4H_2O$. — The i.r. spectra of this salt were dissimilar from those of the calcium halide complexes; thus, the octa-coordination around the calcium ion is completed by two, chelated, acid anions (through O-6 and O-5 or O-6′) and four water molecules, as shown in Scheme 1. This arrangement is rather different from that of the structurally characterized Ca(D-glucuronate)Br · $3H_2O$ complex[7]. The symmetric and antisymmetric stretching-vibrations of the CO_2^- group, together with those of the COH bending and CO stretching vibrations, appeared as broad and strong absorption bands in the spectra of this calcium salt. These obscured the sharp and fine vibrations of the sugar ring, so that it was not possible to make complete assignments.



Scheme 1

The Ca–O stretching vibration[17] of the sugar would occur at a range (300–200 cm^{-1}) lower than that studied here.

CONCLUSIONS

On the basis of the spectroscopic and structural properties of D-glucuronic acid and its calcium complexes, the following conclusions may be drawn:

(*a*) The strong, intermolecular hydrogen-bonding network of the free sugar is retained upon complexation, whereas the intramolecular hydrogen-bonding of the free acid is lost upon metalation.

(*b*) The CO_2^-, CO, and OH groups of the sugar residue, as well as the water molecules, are involved in metal–ligand bonding.

(*c*) The α anomer of the acid is preponderant in these calcium complexes in the solid state.

(*d*) The structure of Ca(D-glucuronate)$_2$ · $4H_2O$ is different from the structures of the corresponding calcium halide complexes; different coordination-sites are involved.

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