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INFRARED SPECTRA OF CRYSTALLINE β-D-GLUCURONIC ACID AND ITS Na^+, K^+, AND Rb^+ SALTS

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ABSTRACT

The infrared spectra of D-glucuronic acid and three of its alkali-metal salts have been recorded. The salts have the formula M D-glucuronate · 2 H_2O, where M = Na^+, K^+, and Rb^+. The structurally known K D-glucuronate · 2 H_2O and its isomorphous Rb D-glucuronate · 2 H_2O salt show that each metal cation has sixfold coordination, surrounded by O-1, O-3, O-6, and O-7 of the D-glucuronate residue, as well as by two oxygen atoms of the water molecules. The crystal structure has an extensive hydrogen-bonding network, and there are binding forces between the positive ion and the electronegative oxygen atoms.

Spectroscopic and other evidence presented here indicated that these three D-glucuronate salts are isomorphous, in terms of common coordination geometry and similar binding-sites involved. The strong hydrogen-bonding system of the free sugar is retained upon ionization, and, in this series of alkali-metal salts, the sugar moiety crystallizes as the β anomer.

INTRODUCTION

Metal–sugar interaction has been known for a long time[1], and X-ray studies[2] or n.m.r. spectroscopy[3–6] have been widely used to characterize the nature of the metal–sugar bondings, but reliable correlation between the structural information and the spectral properties for carbohydrates is still lacking. Recently, correlation between spectral changes and the coordination sites used by the sugar moieties in a series of metal–sugar complexes has been demonstrated[7,8]. Evidence for this came through comparison of the i.r. spectra of the structurally known Ca(D-glucuronate)Br · 3 H_2O (ref. 9) and the Ca(α-L-arabinose)Cl_2 · 4 H_2O (ref. 10) complexes with those of the corresponding free sugars and of other calcium compounds.

In the present work, as there was unambiguous, structural information[11] on K D-glucuronate · 2 H_2O, the i.r. spectrum of this salt was examined, in order to

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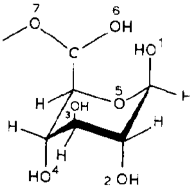
detect the characteristic features of each structural type of the compounds studied here for Na^+ and Rb^+ ions, and to establish a correlation between the spectral changes and the binding sites used by the β-D-glucuronate residue (**1**).



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EXPERIMENTAL

General. — All chemicals were reagent grade and used without further purification. D-Glucuronic acid was BDH reagent-grade, and was recrystallized from water by slow evaporation.

Preparation of D-*glucuronic salts.* — The alkali-metal salts were prepared[11] by addition of D-glucuronic acid (1 mmol) in H_2O (20 mL) to a solution of the metal carbonate (1 mmol) in H_2O (20 mL). The solution was then decolorized by means of activated carbon, concentrated at room temperature, and allowed to crystallize in an atmosphere of ethyl alcohol in a desiccator. The colorless crystals that were formed were washed several times with cold alcohol, dried over $CaCl_2$, and analyzed; they had the empirical formula M D-glucuronate · 2 H_2O, where M = Na^+, K^+, or Rb^+.

Physical measurements. — The infrared spectra were recorded, for KBr pellets, with a Digilab FTS 15/C, Fourier-transform, Michelson infrared interferometer equipped with a high-sensitivity HgCdTe detector and a KBr beam-splitter having a spectral resolution of 4 to 2 cm^{-1}. X-Ray powder photographs were taken for comparative purposes, using a powder camera (Philips, Debye–Scherrer) with CuKα radiation. Conductance measurements were conducted at room temperature for aqueous solutions (mM) with a conductivity meter, type CDM2e (Radiometer, Copenhagen).

RESULTS AND DISCUSSION

Structural analysis had shown[11] that the K^+ ion has sixfold coordination, sited in the vicinities of O-6, O-7, O-3, and O-1 of the D-glucuronate anions and of two oxygen atoms of the water molecules, in the K β-D-glucuronate · 2 H_2O salt. The interaction between the oxygen atoms and the potassium is largely electrostatic, with a K^+–O distance ranging from 279 to 285 pm. A strong hydrogen-bonding network covers the entire crystal structure, and causes stabilization of the structure of the salt. There are two other glucuronate oxygen atoms (O-4) near each potassium ion, with K^+–O bond-lengths of ~300 pm, which are not considered to be part of the sixfold coordination of the potassium ion.

X-Ray powder photography shows that the Na^+, K^+, and Rb^+ glucuronates are isomorphous, in terms of a similar structural arrangement around the metal cations. The observed molar conductivities (80–100 $\Omega^{-1}.mol^{-1}.cm^2$) indicate 1:1 electrolytes for these alkali-metal salts.

The i.r. spectra of these salts, together with that of the free sugar acid have been recorded in the region of 4000–400 cm^{-1}, and the results are discussed in two parts: (*a*) 3700–2700 cm^{-1}, and (*b*) 1800–400 cm^{-1}. It should be noted that this discussion, largely based on the assignments and the normal-coordinate analysis conducted by Hineno[12] and Vasko *et al.*[13], is in good agreement with their observations.

(a) 3700–2700 cm^{-1}. In this region, the free sugar acid shows four major groups of strong absorption bands (each of which has several components) centered at ~3400, 3280, 3160, and 2900 cm^{-1} (see Fig. 1). The first three absorption bands are assigned to the hydrogen-bonded, OH stretching-frequencies[12,13], whereas the fourth absorption band is related to the C–H vibrational frequencies[12,13] (see Table I). The OH stretching-vibrations of the free acid are shifted to higher frequencies in the spectra of the metal D-glucuronates, and a new absorption band also appears, at ~3350 cm^{-1}, in the spectra (see Fig. 1). The shift of the OH

Fig. 1. Infrared spectra of D-glucuronic acid and potassium D-glucuronate in the region of 3700–2700 cm^{-1}. (a, D-Glucuronic acid; b, K D-glucuronate · 2 H_2O.)

TABLE I

INFRARED ABSORPTION BANDS[a] (cm^{-1}) OF CRYSTALLINE D-GLUCURONIC ACID AND ITS ALKALI-METAL SALTS

D-*Glucuronic acid*	*Na* D-*glucuronate* · $2 H_2O$	*K* D-*glucuronate* · $2 H_2O$	*Rb* D-*glucuronate* · $2 H_2O$	*Possible assignments*
3450 sh	3605 s	3580 m	3540 m	νOH (hydrogen-bonding)[12,13]
3400 b	3472 s	3520 b	3462 s	
—	3350 s	3355 s	—	
3280 s	3300 s	3290 s	3280 s	
3160 b	3144 s	3114 s	—	
—	3030 m	—	3020 m	
2926 m	2922 m	2930 w	2917 s	νCH[12,13]
2887 s	2900 w	2900 w	2900 sh	
2840 m	2842 m	2848 m	2870 w	
2766 w	2780 w	2738 w	2780 w	
—	2720 vw	—	—	
1707 s	—	—	—	νC=O[14]
—	1644 sh	1630 sh	—	δH_2O[16]
—	1600 bs	1592 vs	1606 bs	νOCO$^-$ antisymmetrical[16]
—	1473 m	1465 sh	1495 m	νOCO$^-$ symmetrical[16]
1457 s	1429 s	1432 s	1413 s	δ(OCH) + δ(CCH)[12,13]
1363 sh	1383 m	1384 m	1365 w	δ(CCH) + δ(COH)[12,13]
1345 s	1339 m	1349 m	1335 m	δ(CCH) + δ(COH)[12]
1325 s	—	1324 m	1317 sh	δ(CCH) + δ(COH) + δ(OCH)[12]
1300 sh	1300 m	1300 m	1292 s	
1259 s	1255 w	1263 m	1269 sh	δ(CCH) + δ(COH)[12]
1227 s	1238 w	1225 w	1227 w	δ(COH) + δ(CCH)[12]
1205 m	1193 w	1203 w	1190 vw	
1159 s	1167 s	1161 w	1160 s	ν(CO) + ν(CC) + δ(CCC)[12]
1140 s	1129 sh	—	1126 sh	ν(CO) + ν(CC) + δ(CCO)[12]
1100 sh	1115 m	1111 vs	1106 m	
1089 vs	1070 vs	1072 vs	1088 m	ν(CC) + ν(CO)[12]
1046 sh	1043 s	1063 vs	1056 vs	ν(CO) + δ(CCO) + δ(CC)[12]
1024 vs	1022 s	1019 vs	1022 vs	
960 sh	960 vw	—	—	ν(CO) + δ(CCH)[12]
944 m	945 w	947 m	942 m	
900 vw	—	890 vw	900 sh	ν(CC) + δ(CCH) + δ(CO)[12]
770 m	786 w	798 w	792 m	τ(CO) + δ(CCO) + δ(CCH)[12]
740 m	737 m	738 m	753 m	
715 s	—	—	—	(CCO) + (OCO) + τ(CO)[12]
680 m	678 m	677 m	—	δ(CCO) + τ(CCO)[12]
—	670 w	—	667 m	
600 w	611 w	—	597 m	τ(CO)[12]
580 m	584 m	577 w	577 m	
570 m	—	557 vw	557 w	τ(CO) + δ(CCO)[12]
560 m	—	—	545 vw	
530 m	537 w	520 s	538 m	
480 w	499 w	—	—	δ(CCO) + ν(CO)[12]
460 m	—	—	—	
450 m	452 m	—	—	
430 w	—	437 w	445 w	δ(CCO) + δ(CCH)[12]
420 w	—	—	—	

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

stretching-vibrations towards higher frequencies is indicative of weakening of the strong, hydrogen-bonding network of the free acid upon ionization, whereas the presence of the new band at 3350 cm^{-1} is mainly due to the water molecules and to rearrangement of the hydrogen-bonding system of the sugar moiety in the crystal structures[11] of these alkali-metal salts.

A band having medium intensity, at 3450 cm^{-1}, in the spectrum of the free acid, assigned to a weakly hydrogen-bonded OH group[14], appeared as a sharp absorption band at 3605 cm^{-1} in the spectrum of sodium D-glucuronate. The shift observed could be related to the presence of a free OH group[15] of the D-glucuronate residue in this salt. The C-H stretching vibrations of the free acid at ~2900 cm^{-1} showed no considerable changes upon sugar metalation (see Table I). The main features of the spectra, as related to this discussion, with the possible assignments, are given in Table I and Fig. 1.

(b) 1800–400 cm^{-1}. Although the interaction between the alkali cations and the D-glucuronate anion was found[11] to be largely ionic, the ionization of the free acid causes drastic spectral changes in this region of the spectra. The atomic motions of the sugar ring are strongly coupled, and the vibrations are spread over the entire molecule, so that the individual assignment for each absorption band is difficult to make. Metalation or ionization of the acid moiety can also change the electron distribution within the ring system, and this modifies the vibrational frequencies. However, some of the most common and meaningful spectral changes observed are summarized next.

A strong absorption band at 1707 cm^{-1} in the spectrum of the free acid, assigned to the C=O stretching vibration[14], was shifted to a lower frequency and split into two components, at ~1600 and 1500 cm^{-1}, in the spectra of the alkali-metal salts (see Fig. 2 and Table I). These absorption bands are respectively related to the antisymmetrical and symmetrical stretching-vibrations of the COO^-group[16]. It has been suggested[16] that, in a series of metal carboxylate complexes, the separation between the symmetrical and the antisymmetrical component of the COO^- group is a measure of the chelation or the bridging of the carboxylate anion. In the calcium D-glucuronate compounds reported earlier[7], containing chelation or a bridging metal carboxylate group, the separation of the COO^- splitting was 150 cm^{-1}. It has been found[11] that the alkali metal–D-glucuronate interaction is largely ionic, but the separation of ~100 cm^{-1} for the two COO^- components is indicative of some degree of direct metal–oxygen interaction, in these series of D-glucuronates. Similar interaction was observed[17–19] for potassium–oxygen bonding having a similar K^+–O distance (275 to 290 pm) in a series of potassium salts containing carboxylate anions and a neutral sugar molecule. It is worth noting that the COO^- group is a stronger hydrogen-bonding donor than the parent COO–H group. Therefore, the rearrangement of the hydrogen-bonding network of the free acid would also affect the COO^- stretching-vibrations upon ionization. A shoulder absorption-band at ~1630 cm^{-1} appeared in the spectra of the sodium and potassium salts, and it was assigned to the bending vibration of the water molecule[16]. Such an

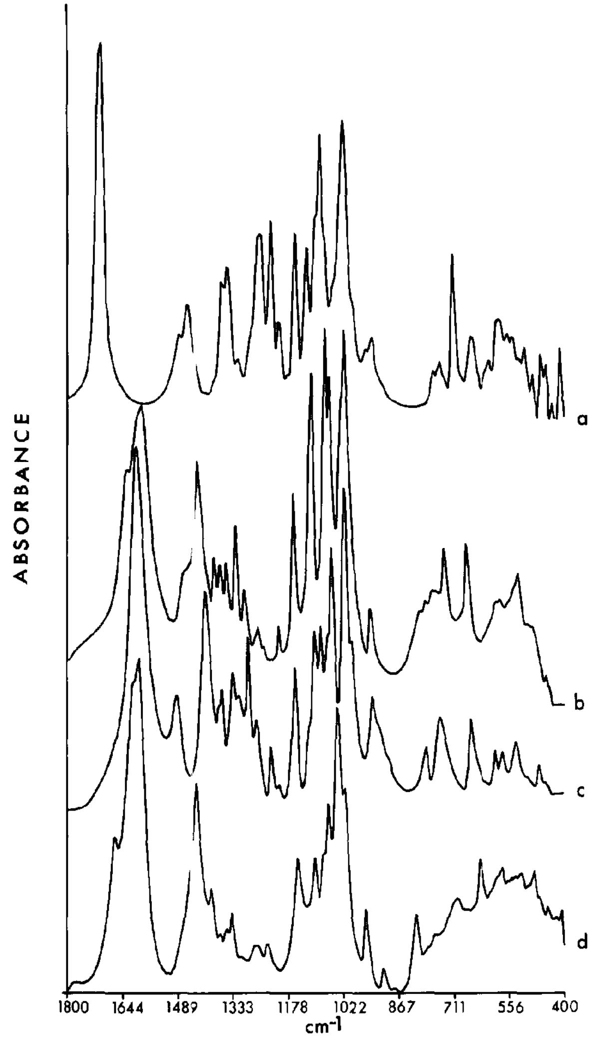

Fig. 2. Infrared spectra of D-glucuronic acid and of three metal D-glucuronates in the region of 1800–400 cm^{-1}. (a, D-Glucuronic acid; b, K D-glucuronate · 2 H_2O; c, Rb D-glucuronate · 2 H_2O; and d, Ca(D-glucuronate)Br · 3 H_2O.)

absorption band at 1630 cm^{-1}, and another at 3350 cm^{-1} related to the presence of the H_2O molecules, were not observed in the spectrum of the corresponding rubidium salt, mainly due to the gradual dehydration of this salt upon air drying, as reported earlier[11].

In the spectrum of the free acid, seven absorption bands, at 1457, 1365, 1325, 1300, 1259, 1227. and 1205 cm^{-1}, mainly assigned to the bending vibrations[12,13] of the COH and CCH groups, show considerable changes in intensity, and are shifted to lower frequencies (see Fig. 2 and Table I). The shifts of the COH bending to lower frequencies, together with those of the OH stretchings at 3600–3200 cm^{-1} to higher frequencies, are indicative of the general weakening of the hydrogen-bonding system of the free acid, and the possible metal–oxygen interaction of the sugar hydroxyl groups, upon salt formation. Other absorption bands, at ~1205, 1159, 1140, 1100, 1089, 1046, 1024 and 940 cm^{-1}, in the spectrum of the free acid, are assignable mainly to shift of the C–O stretching vibrations[12] to lower frequencies upon sugar metalation (see Table I). The shifts of the C–O stretching vibrations towards lower frequencies are due to rearrangement of the strong, hydrogen-bonding network of the glucuronate moiety and to the direct metal–oxygen interaction upon acid ionization[16].

The skeletal deformations at ~1100–400 cm^{-1} in the spectrum of the free acid showed considerable changes on metalation. The bands, having medium intensities, at 770 and 740 cm^{-1} appeared as sharp absorption bands at higher frequencies in the spectra of the alkali-metal salts (see Table I). A sharp absorption band at 715 cm^{-1} in the ligand spectra disappeared upon acid ionization (see Fig. 2), and a band at 680 cm^{-1} in the spectrum of the free acid, shifted to a lower frequency upon sugar metalation (see Table I). Because these vibrations are mainly related to the C–C–C, C–O–C, and O–C–O skeletal deformations[12], it seems that the ionization of the free acid can change the electron distribution within the ring system, where the vibrations are mostly localized, causing ring distortion and finally modifying these vibrational frequencies. It should also be noted that the rearrangement of the strong hydrogen-bonding system of the free acid can affect the skeletal vibrations upon metalation.

α and β Anomers. Structural data showed[11] that the D-glucuronate anion crystallizes as the β anomer in the crystal structure of the alkali-metal salts, whereas the α anomer preponderates in the crystal structure[9] of Ca(D-glucuronate) Br · 3 H_2O. It has also been suggested[4] that the β anomer of D-glucuronic acid preponderates in aqueous solution, and that calcium cations show different affinities for the α and β anomers of certain sugars in solution. Previously, there were reported[7] the i.r. spectra of D-glucuronic acid and its calcium complexes, in which a sharp absorption band appeared at 825 cm^{-1}, also found in the spectra of the structurally known Ca(D-glucuronate)Br · 3 H_2O and of the corresponding chloride, but absent from the spectrum of the free acid, which was attributed to the presence of the α anomer[20,21] of the D-glucuronate residue in those calcium–sugar complexes (see Fig. 2). In the present work, the absence of this band at 825 cm^{-1} from the spectra of the alkali-metal salts is indicative of the presence of the D-glucuronate anion as the β anomer in this series of metal D-glucuronates (see Fig. 2), which is consistent with the structural analysis[11] for K D-glucuronate · 2 H_2O.

CONCLUSIONS

Although Raman and infrared techniques have often been used to characterize the vibrational frequencies of sugars, a reliable correlation between the structural properties and spectroscopic information for carbohydrates is still hard to establish. Metalation of the glycuronic moieties can provide a useful probe in order to develop our understanding about vibrational problems for carbohydrates. Hence, using the spectroscopic and structural properties of D-glucuronic acid and its alkali-metal salts studied here, the following conclusions may be reached.

(*a*) The strong hydrogen-bonding system of the free acid is preserved upon ionization; (*b*) there is some degree of direct interaction between these metal cations and the COO^-, CO, and OH groups of the D-glucuronate anion; (*c*) the sugar moiety crystallizes as the β anomer in these alkali-metal salts; and (*d*) the Na^+, K^+, and Rb^+ salts are isostructural, in terms of similar coordination number and common binding-environments.

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