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SUGAR ADDUCTS WITH ALKALINE EARTH METAL IONS

INTERACTION OF L-ARABINOSE WITH Sr(II) AND Ba(II) IONS AND THE EFFECTS OF METAL ION BINDING ON THE SUGAR ANOMERIC CONFIGURATIONS

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The reaction between L-arabinose and hydrated Sr(II) and Ba(II) halide salts has been studied in H_2O solution and adducts of the type M(L-arabinose)$X_2 \cdot 4H_2O$, where M = Sr(II) or Ba(II) and X = Cl^- or Br^- have been isolated and characterized by means of Fourier transform infrared spectroscopy, ^{1}H-NMR spectroscopy, molar conductivity and X-ray powder diffraction measurements. Due to the marked spectral similarities with those of the structurally known Ca(L-arabinose)$X_2 \cdot 4H_2O$ (X = Cl^- or Br^-) compounds, the Sr(II) and the Ba(II) ions are eight-coordinated, binding to two L-arabinose molecules via O1, O5 of the first and O3, O4 of the second sugar moiety and to four H_2O molecules. ^{1}H-NMR spectroscopy indicated that the free L-arabinose has the β-anomer configuration in aqueous solution, whereas the α-anomer isomer is preferred by Mg(II), Ca(II), Sr(II) and Ba(II) ions, on complexation.

1. Introduction

Recent discovery of the carbohydrate-metal complexes in the human body [1,2] has demonstrated the importance of sugar-metal interaction. Ni(II) was found to interact with several sugar moieties in human kidney [1,2]. Ca^{2+} and sugars appear to participate in a variety of biological adhesion and agglutination processes, particularly those occurring at cell surfaces [3]. On the other hand, metal ion interaction with nucleic acids plays an important role in DNA conformational transitions [4]. Sugar is a component part of the nucleic acid and sugar-metal ion interaction has significant biological importance.

Recently, we have reported the complexation of L-arabinose with the calcium [5], magnesium [6], uranium [7] and the zinc group metal ions [8]. The binding of these metal cations took place via sugar hydroxyl groups of the α-anomeric sugar configuration, while the β-anomer was predominant for the uncomplexes sugar molecule [5–8]. In this work, we describe the interaction of L-arabinose with Sr(II) and Ba(II) ions in aqueous solution and the isolation and characterization of several metal-arabinose adducts, using Fourier transform infrared spectroscopy (FT-IR), ^{1}H-NMR spectroscopy, molar conductivity and X-ray powder diffraction measurements that have not been previously reported. The spectroscopic properties of these metal-sugar adducts have been compared with those of the structurally characterized Ca-arabinose [5,9], Mg-arabinose [6], UO_2-arabinose [7] and the zinc group metal-arabinose complexes [8]. This comparison allowed us to detect the characteristic features of each structural type of adduct synthesized for strontium and barium ions

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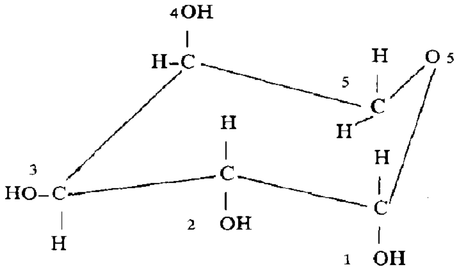
and to establish a correlation between the spectral changes and the sugar-binding sites involved. Furthermore, the effects of these metal ions' coordination on the sugar anomeric changes is discussed here. The chemical structure of L-arabinose with the numbering of the atoms is shown below.



L-Arabinose

2. Experimental

2.1. Materials and methods

L-Arabinose was obtained from BDH and was recrystallized from a water/methanol mixture. All other chemicals were of reagent grade and used as supplied.

2.2. Synthesis of metal-sugar adducts

Alkaline earth metal halide salt, 0.02 mol in H_2O (30 ml), was added to a hot solution of L-arabinose, 0.01 mol in H_2O (20 ml), and the solution mixture was heated up to 80°C for 1 h. After cooling down the solution to room temperature, it was left for a period of 1 week under slow evaporation. Colorless crystals were deposited and then filtered off and washed with ethanol several times and dried over $CaCl_2$. The analytical results showed compositions of Sr(L-arabinose)$X_2 \cdot 4H_2O$ and Ba(L-arabinose)$X_2 \cdot 4H_2O$, where X-Cl^- or Br^-. These compounds are very soluble in water but not soluble in other common organic solvents.

2.3. Physical measurements

^{1}H-NMR spectra were recorded on a Bruker WH-90 MHz instrument with ^2H_2O solution containing DSS as reference. Infrared spectra were taken on a Digilab FTS 15/C Fourier transform Michelson infrared interferometer, equipped with a high-sensitivity HgCdTe detector and a KBr beam splitter, with spectral resolution of 4–2 cm^{-1} and KCl pellets. X-ray powder photographs were taken for comparative purposes, using a camera (Phillips-Debye-Scherre) with copper K_α radiation and nickel filter. Molar conductance measurements were carried out at room temperature in H_2O solutions (10^{-3} M) with a type CDM2e conductivity meter (Radiometer, Copenhagen).

3. Data and discussion

X-ray structural information and spectroscopic properties of Ca(L-arabinose)$X_2 \cdot 4H_2O$ and the Mg(L-arabinose)$X_2 \cdot 4H_2O$ ($X = Cl^-$ or Br^-) showed that the Ca(II) ion is eight-coordinated, binding to two arabinose molecules through O1, O5 of the first and O3, O4 of the second and to four water molecules, whereas the Mg(II) ion is six-coordinated, binding to two sugar moieties and to two H_2O molecules [5,6,9]. The strong sugar intermolecular hydrogen-bonding network was altered to that of the sugar-OH...H_2O...halide system [9], upon sugar metalation. On the other hand, on the basis of the spectroscopic studies it was concluded that the uranium ion and the zinc group metal cations are also six-coordinated, binding to two arabinose molecules similar to that of the Mg(II) ion, in M(L-arabinose)$X_2 \cdot 2H_2O$ (M = Zn(II), Cd(II) and UO_2^{2+} and $X = Cl^-$ or Br^-) compounds [7,8]. The FT-IR spectra of these metal-sugar adducts have been recorded in the region 4000–500 cm^{-1} and compared with those of the Sr(II)- and Ba(II)-arabinose compounds studied here. The results of the spectral analysis will be discussed below:

3.1. L-Arabinose OH stretching vibrations and binding modes

The assignments of the L-arabinose OH stretching vibrations have been discussed in our earlier report [8]. On the basis of the intermolecular O...O distances obtained from X-ray [10] and neutron diffraction measurements [11] summarized below, the following relationships are present in the free L-arabinose hydrogen-bonding structure.

O(2)–H > O(3)–H > O(1)–H > O(4)–H.

Hydrogen bond	O…H (Å)	O…O (Å)	ν OH (cm^{-1})
O(2)–H…O(3)H	1.735	2.680	3235 b
O(3)–H…O(2)H	1.801	2.747	3321 sh
O(1)–H…O(5)	1.820	2.762	3340 vs
O(4)–H…O(2)H	2.201	3.020	3536 s

Therefore, the four strong absorption bands observed in the infrared spectrum of free L-arabinose are assigned to the strongly hydrogen-bonded O(2)–H (3235 cm^{-1}), O(3)–H (3321 cm^{-1}), O(1)–H (3340 cm^{-1}) and the unperturbed O(4)–H (3536 cm^{-1}) stretching frequencies (table 1).

Upon alkaline earth metal ion interaction, the free sugar OH stretching vibrations exhibited major intensity changes and shifted towards

Table 1

FT-IR absorption bands (cm^{-1}) for L-arabinose and its alkaline earth metal ion adducts in the region 4000–500 cm^{-1} with possible assignments

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

L-Arabinose	Sr(L-arabinose)$Cl_2 \cdot 4H_2O$	Sr(L-arabinose)$Br_2 \cdot 4H_2O$	Ba(L-arabinose)$Cl_2 \cdot 4H_2O$	Ba(L-arabinose)$Br_2 \cdot 4H_2O$	Assignments [4,6–10]
3536 s	3520 s	3525 s	3525 s	3520 s	νO(4)–H…O2
3340 vs	3280 s	3290 vs	3275 s	3295 s	νO(1)–H…O5
3321 sh	3300 s	3315 s	3310 s	3300 s	νO(3)–H…O2
	3285 s	3290 s	3275 s	3285 s	
3235 b	3215 s	3220 s	3210 s	3210 vs	νO(2)–H…O3
2995 w	2990 w	2995 w	2990 w	2990 vw	$\nu as(CH_2)$ of C_5
2970 sh	2975 sh	2970 sh	2975 m	2970 m	ν(CH) of C4
2953 m	2950 w	2955 w	2955 m	2950 w	ν(CH) of C3
2940 m	2940 m	2935 w	2945 w	2940 m	ν(CH) of C2
2891 w	2890 vw	2895 w	2895 w	2895 w	$\nu s(CH_2)$ of C5
2864 vw	–	–	–	–	ν(CH) of C1
	1645 bm	1640 bm	1645 bm	1645 bm	$\delta(H_2O)$
1473 m	1460 sh	1465 sh	1460 m	1465 m	δ(COH) + δ(CCH)
1425 w	1445 m	1447 w	1440 m	1445 m	δ(COH) + δ(CCH)
1402 vw	1400 w	1405 m	1395 w	1400 m	$\delta(CH_2)$ + δ(COH)
1371 s	1385 w	1375 m	1380 m	1375 m	$\delta(CH_2)$ + δ(COH)
1357 m	1355 m	1349 m	1350 m	1345 m	δ(CCH) + δ(COH)
1317 s	1320 w	1317 w	1320 sh	1320 m	δ(CCH) + δ(COH)
1257 m	1270 m	1275 m	1265 sh	1268 m	δ(CCH) + δ(COH)
1232 m	1230 s	1225 m	1225 s	1230 s	δ(COH) + δ(CCH)
1134 m	1138 sh	1150 s	1145 s	1140 s	ν(CO) + ν(CC)
1100 sh	–	–	–	–	ν(CC) + ν(CO)
1092 s	1095 s	1099 s	1100 s	1090 s	ν(CC) + ν(CO)
1069 s	–	–	–	–	ν(CO)
1053 vs	1063 s	1060 s	1055 s	1060 s	ν(CO)
1002 s	1000 s	1003 s	1000 s	1000 s	ν(CO) + δ(CCO)
943 m	940 m	945 m	945 m	940 m	δ(CCH) + ν(CO)
893 s	900 m	895 m	890 m	890 m	ν(CC) + δ(CH)
842 s	844 m	845 m	845 m	845 m	δ(CH)
785 s	780 m	790 s	789 m	790 s	τ(CO) + δ(CCO)
713 m	710 m	712 m	705 m	710 m	δ(CCO) + δ(OCO)
677 s	670 m	675 m	670 m	671 m	δ(CCO) + δ(CO)
627 w	620 m	625 m	622 m	620 m	δ(CO)
602 m	600 m	602 w	599 w	600 m	τ(CO) + δ(CCO)
590 m	590 w	586 m	590 m	599 w	τ(CO) + δ(CCO)
530 vw	540 w	535 w	540 w	535 vw	δ(CCO) + δ(CCC)

lower frequencies (table 1). The observed spectral changes are related to the participation of the sugar OH groups in complex formation. It should be noted that similar spectral changes were observed in the infrared spectra of the known Ca(II)- and Mg(II)-arabinose adducts [5,6], where each metal ion was found to be bonded to two sugar moieties through sugar hydroxyl groups O3, O4 of the first and O1, O5 of the second molecule [9]. Therefore, the binding of the L-arabinose molecules is similar in these Sr(II)- and Ba(II)-sugar compounds.

It is worth mentioning that the alterations of the free sugar hydrogen-bonding network to that of the sugar-OH... H_2O...halide system, that is reported in the crystal structure of the Ca(L-arabinose)$Cl_2 \cdot 4H_2O$ compound [9], are also responsible for modifications of the sugar hydroxyl stretching vibrations. However, it is rather difficult to separate the effects of metal coordination and the change of the hydrogen-bonding network on the sugar OH stretching frequency.

3.2. H_2O coordination

Due to the overlapping of the sugar OH stretching vibrations with that of the bonded H_2O molecule in the region 3500–3200 cm^{-1}, it is difficult to draw a definite conclusion as to the nature of the metal-H_2O bonding. However, the presence of a broad absorption band with medium intensity at about 1645 cm^{-1} in the spectra of the Sr(II)- and Ba(II)-arabinose adducts, which is absent in the free sugar spectrum (table 1), was assigned to the bending mode of the bonded water molecule [5,6].

3.3. L-Arabinose C–H stretching vibrations

The assignments of the L-arabinose C–H stretching vibrations have been previously reported by us [8] and Szarek et al. [12]. L-Arabinose has six fundamental C–H stretching vibrations and the six absorption bands with medium intensities observed at about 3000–2800 cm^{-1} in the infrared spectrum of the free L-arabinose studied here are assigned to the antisymmetric and symmetric CH_2 and CH stretching vibrations (table 1). The C–H stretching vibrations of the free sugar showed no major changes upon adduct formation (table 1).

3.4. L-Arabinose ribose ring vibrational frequencies and metal binding

The ribose ring vibrational frequencies are strongly coupled and assignment of each absorption band to a particular vibration is difficult to make. However, metalation of the free sugar molecule led us to the following observations.

Several absorption bands with medium intensities in the region 1470–1230 cm^{-1} in the free sugar spectrum are assigned to the strongly coupled COH, CCH and CH_2 deformation modes [13,14] and exhibited major intensity changes and shifting towards higher frequencies, upon complexation (table 1). The spectral changes observed for the COH bendings together with the shifts of the OH stretching vibrations at 3500–3200 cm^{-1} are indicative of the participation of the sugar hydroxyl groups in metal adduct formation [7,8].

The CO stretching vibrations of the ribose ring appeared as several strong absorption bands at about 1100, 1092, 1069, 1053, 1002 and 943 cm^{-1} in the free arabinose spectrum and showed considerable intensity changes and shifted towards lower frequencies in the spectra of these metal-sugar compounds (table 1). The observed spectral changes are due to the CO group involvement in metal-sugar bondings [5,6]. These observations are consistent with the structural information reported for Ca(L-arabinose)$Cl_2 \cdot 4H_2O$, which showed the participation of the sugar CO and OH groups in metal complex formation [9].

The ribose ring skeletal deformations C–O–C and C–C–C [13,14] observed in the region 900–500 cm^{-1} for free L-arabinose showed major alterations upon sugar metalation (table 1). The changes observed are related to the metal-sugar coordination, which perturbs the electron distribution within the ring system, where the vibrations are mostly localized and finally brings about the ring distortion [5–8].

3.5. ^1H-NMR and sugar anomeric changes

The ^1H-NMR spectra of D-arabinose have been studied by Lemieux and Stevens [15]. The anomeric proton (H_1) chemical shifts of the free L-arabinose studied here were observed at 5.22 ppm for the β-anomer and 4.50 ppm for the α-anomer (in ^2H_2O) and showed major changes upon sugar metal interaction (fig. 1). The observed downfield shifts of the anomeric proton chemical shifts are related to the participation of the sugar O(1)-H group in metal-ligand bonding (fig. 1). It is important to note the drastic changes observed for the ratio of the anomeric sugar configurations, on complex formation, which are summarized below:

Compound	α/β (%)
Free L-arabinose	48/52
Mg(L-arabinose)$Cl_2 \cdot 4H_2O$	59/41
Mg(L-arabinose)$Br_2 \cdot 4H_2O$	58/42
Ca(L-arabinose)$Cl_2 \cdot 4H_2O$	68/32
Ca(L-arabinose)$Br_2 \cdot 4H_2O$	64/36
Sr(L-arabinose)$Cl_2 \cdot 4H_2O$	63/37
Sr(L-arabinose)$Br_2 \cdot 4H_2O$	60/40
Ba(L-arabinose)$Cl_2 \cdot 4H_2O$	61/39
Ba(L-arabinose)$Br_2 \cdot 4H_2O$	68/32

From the ^{1}H-NMR results obtained here for alkaline earth metal-arabinose adducts, it is obvious that the free sugar has the β-anomer configuration, while the α-anomer is preferred, upon complexation (fig. 1). The sugar β-anomer to α-anomeric changes are due to the chelation of L-arabinose molecule via O1 and O5 oxygen atoms, which required the β- to α-anomeric changes. The results are consistent with the X-ray structural information reported for Ca(L-arabinose)$Cl_2 \cdot 4H_2O$, which showed the participation of the sugar O(1)-H group in adduct formation and the crystallization of -arabinose in its α-anomer form, in this calcium-sugar compound [9]. Similar ^{1}H-NMR spectral changes were observed for the uranium and zinc group metal-arabinose compounds [7,8], where the β-anomer to α-anomer isomeric changes were observed, upon sugar metalation.

3.6. X-ray diffraction measurement and molar conductivity

The X-ray powder diagrams of the Sr(II) and Ba(II)-arabinose adducts were similar to those of the structurally identified Ca(L-arabinose)$Cl_2 \cdot 4H_2O$ [9], which is indicative of a similar coordination number (C.N. = 8) and similar binding

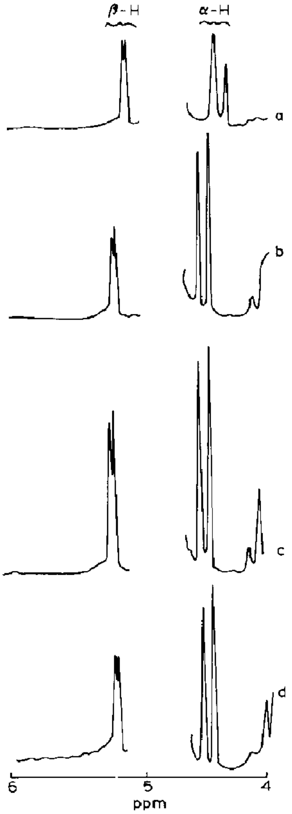


Fig. 1. ^{1}H-NMR chemical shifts of the anomeric proton (H_1) in ^2H_2O solution for: a, free L-arabinose; b, Ca(L-arabinose)$Cl_2 \cdot 4H_2O$; c, Sr(L-arabinose)$Br_2 \cdot 4H_2O$; d, Ba(L-arabinose)$Cl_2 \cdot 4H_2O$.

arrangements around these alkaline earth metal-sugar complexes. On the other hand, the X-ray powder patterns of the Mg-arabinose adducts showed no marked similarities with those of the strontium and barium-arabinose adducts and this is mainly due to the smaller coordination number (C.N. = 6), which was found for the Mg(II) ion with respect to the other alkaline earth metal ions [16].

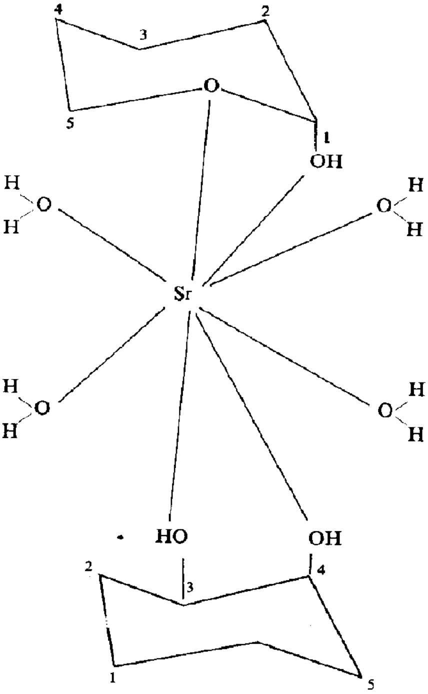
The high molar conductivities (180–200 Ω^{-1} cm^2 mol^{-1}) observed for Sr(II)- and Ba(II – arabinose compounds in aqueous solutions are indicative of the dissociation of these metal-sugar adducts in H_2O solutions and the presence of no direct metal-halide interaction, in these series of alkaline earth metal-sugar compounds. The results are consistent with the analysis of the Ca(L-arabinose)$Cl_2 \cdot 4H_2O$ compound [9], which showed no direct calcium-halide interaction.

4. Concluding remarks

On the basis of the FT-IR, ^{1}H-NMR spectroscopy and X-ray powder diffraction measurements of the Sr(II)- and Ba(II)-arabinose adducts and the comparisons made with the other structurally known metal-arabinose compounds, the following points can be emphasised:

(a) The strong sugar intermolecular hydrogen-bonding network is altered to that of the sugar-OH...H_2O...halide system, on complex formation;

(b) Sr(II) and Ba(II) ions bind to two arabinose molecules via O1, O5 of the first and O3, O4 of the second as well as to four H_2O, resulting in an eight-coordination geometry around these metal ions (scheme A);



Scheme A. Metal-arabinose adduct.

(c) The free L-arabinose has the β-anomer configuration in aqueous solution, while the α-anomer is favored, upon alkaline earth metal ion interaction.

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