Carbohydrate Research, 188 (1989) 25–34
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

OXOVANADIUM(IV) AND COPPER(II) COORDINATION BY D-GALACTURONIC AND D-GLUCURONIC ACIDS*

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(Received September 26th, 1988; accepted for publication, December 1st, 1988)

ABSTRACT

Potentiometric and spectroscopic studies show that D-galacturonic and D-glucuronic acids are effective ligands for oxovanadium(IV) ions. The carboxylate group initiates the coordination of the metal ion at pH >3 and one or two deprotonated sugar hydroxyl groups are then involved. The position of HO-4 is critical for the resulting equilibria. Cupric ions interact with ligands in a manner similar to that of oxovanadium(IV), although the stabilities of the corresponding complexes are much lower.

INTRODUCTION

The formation of metal complexes by D-glucuronic or D-galacturonic acid, or polysaccharides containing these moieties, is of biological importance both for essential and toxic metal ions[1–7]. We now report on the oxovanadium(IV) and copper(II) complexes of these simple sugar acids. Earlier studies of the copper(II) complexes are incomplete and the complexes of oxovanadium(IV), which are produced[8,9] in the reaction of sugars with vanadate(V), are almost unknown.

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*Presented at the XIVth International Carbohydrate Symposium, Stockholm, Sweden, August 14–19, 1988.

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EXPERIMENTAL

Materials. — D-Galacturonic acid monohydrate and D-glucuronic acid were commercial samples. $VOSO_4 \cdot 3H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ were used as the sources of the metal ions. Fresh solutions of VO^{2+} (10^{-2}M) were prepared just prior to the spectral measurements. The pH was adjusted, as appropriate, with H_2SO_4 and NaOH. In order to minimise oxidation of oxovanadium(IV) ions in the air, nitrogen or argon was bubbled through the solutions.

Spectroscopic measurements. — Electon paramagnetic (e.p.r.) measurements were carried out with a Varian E-9 spectrometer at the X-band frequency (9.15 GHz) at room temperature, using flat quartz cells sealed under nitrogen, or at 110 K in 3:1 water–ethylene glycol. The electronic spectra were recorded with a Uvidec Jasco 610 spectrophotometer and the c.d. spectra with a Jobin Yvon Mark III spectropolarimeter. 0.01M Solutions of metal ions and a 2:1 or 4:1 ligand-to-metal molar ratio were used.

Potentiometry. — The titration data were collected at 25 ±0.03° with a Tacussel ISIS 2000 pH meter equipped with a TB 10/HA glass electrode and a calomel saturated reference electrode. All titrations were carried out under argon and constant ionic strength (KNO_3). Carbonate-free 0.1M NaOH was used as the titrant. VO^{2+}-containing solutions were obtained by dissolving $VOSO_4 \cdot 3H_2O$ in water. Impurities of vanadium(V) were removed with SO_2. Oxovanadium(IV) chloride was prepared by the addition of barium chloride in stoichiometric amounts. The $VOCl_2$ solutions were standardised with $KMnO_4$. Pure cupric chloride was used to prepare stock 0.2M solutions of copper(II) that were checked by titration with EDTA. The calculations of the stability constants were performed with the SUPERQUAD computer program[10].

Polarography. — A Tacussel PRG5 polarograph was used with a dropping mercury electrode (drop time, 1.5 s), a platinum wire, and a saturated calomel electrode as the working, counter, and reference electrodes, respectively. Measurements were performed at 25° in 0.5M $NaClO_4$ under an argon atmosphere, over the pH range 5.5–6.2. The results are presented in Tables I and II.

TABLE I

HALF-WAVE POTENTIALS ($E_{1/2}$) AND LIMITING CURRENTS (i_l) FOR THE COPPER(II) COMPLEXES WITH D-GLUCURONIC ACID AS A FUNCTION OF THE LIGAND CONCENTRATION [L][a]

[L] (mM)	$E_{1/2}$ (mV)	i_l (mm)
0	+20.0	84
20	+15.0	73
30	+11.5	71
40	+9.0	69
60	+4.0	67
100	−4.0	64
150	−12.0	62
200	−18.5	60.5

[a] [Cu(II)] = 0.1mM and [$NaClO_4$] = 0.5M.

TABLE II

HALF-WAVE POTENTIALS ($E_{1/2}$) AND LIMITING CURRENTS (i_l) FOR THE COPPER(II) COMPLEXES WITH D-GALACTURONIC ACID AS A FUNCTION OF THE LIGAND CONCENTRATION [L][a]

[L] (mM)	$E_{1/2}$ (mV)	i_l (mm)
0	+21.0	93
10	+13.0	81
15	+10.5	79
20	+9.0	77
30	+3.5	75
40	−0.5	72.5
60	−7.5	70
100	−18.0	67.5
150	−27.0	65
200	−34.5	63.5

[a] [Cu(II)] = 0.1mM and [$NaClO_4$] = 0.5M.

RESULTS AND DISCUSSION

D-Galacturonic acid (LH) has a proton dissociation constant (pK_1 3.28) corresponding to the carboxyl group. The dissociation constant of the hydroxyl group with pK_2 ~12.5 cannot be obtained precisely by potentiometry due to low reliability of the pH reading of the glass electrode at pH >11.5. The potentiometric data indicate that, in the VO^{2+}–D-galacturonic acid solutions, three major complexes are formed at pH >4 (Table III, Fig. 1). The computer calculations suggest also the presence of a minor species (12-1), or VOL_2H_{-1}, but its low concentration (<10%) does not allow its existence to be detected by other techniques. The e.p.r. spectra (Fig. 2) record another complex species over the pH range 3.5–5.2, which most likely is the VOL_2 complex in which the metal ion binds two ligands *via* the carboxylate group only (see below for the complexes with D-glucuronic acid). The e.p.r. technique is sensitive to the oxovanadium(IV) coordination mode[11]. The spectroscopic data clearly indicate the formation of the first major complex (12-2) or VOL_2H_{-2} [~100% of the oxovanadium(IV) at pH ~7, see Fig. 1]. In this species, two ligand molecules form chelate rings by coordinating the metal ion through carboxylate and deprotonated hydroxyl groups. Two consecutive proton dissociations from the hydroxyl groups of the coordinated sugar molecules result in the formation of the (12-3) and (12-4) (or VOL_2H_{-3} and VOL_2H_{-4}, respectively) complexes. Although the e.p.r. or other spectroscopic parameters do not distinguish between the (12-3) and (12-4) complexes formed in basic solutions, they clearly indicate that a complex with a coordination mode significantly different than that for the (12-2) species is formed at pH >9. The spectral parameters recorded on solutions at pH >10, in which the only species is the (12-4) complex, are presented in Table IV and Figs. 2 and 3. The significant changes of each spectroscopic parameter when the (12-2) species is transformed into the (12-4) complex indicate

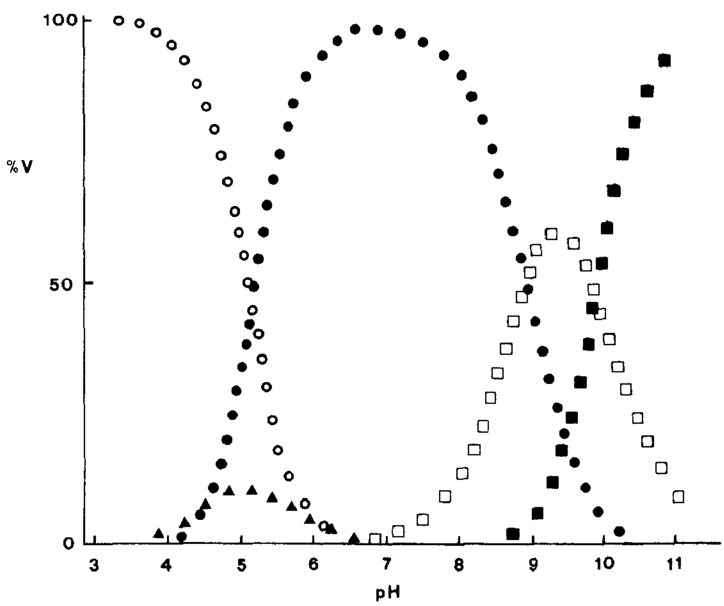

Fig. 1. Species distribution in the VO(IV)–D-galacturonic acid system as a function of pH: VO^{2+} (○), VOL_2H_{-1} (▲), VOL_2H_{-2} (●), VOL_2H_{-3} (□), and VOL_2H_{-4} (■). The metal ion and ligand concentrations are those reported in Table III.

TABLE III

STABILITY CONSTANTS (log β) OF COMPLEX SPECIES WITH D-GALACTURONIC ACID AND D-GLUCURONIC ACID[a]

	p q r	D-*Galacturonic acid*	D-*Glucuronic acid*
	0 1 1	3.280(0.002)	3.061(0.002)
	1 2 0		3.90(0.10)
	1 2–1	0.47(0.14)	
VO^{2+}	1 2–2	−4.01(0.04)	
	1 2–3	−12.98(0.08)	
	1 2–4	−22.91(0.10)	
	0 1 1	3.147(0.003)	3.061(0.002)
	1 2 0	3.00(0.03)	
Cu^{2+}	1 2–1	−3.02(0.08)	−3.03(0.09)
	1 2–2	−10.06(0.10)	
	1 2–4	−29.69(0.20)	

[a] $\beta = [M_pL_qH_r]/[M]^p[L]^q[H]^r$. Standard deviation is given in parentheses. Ionic strength, 0.1 and 1M KNO_3 (for VO^{2+} and Cu^{2+}, respectively). [Cu(II)] = 1.3mM and [L] = 47.2mM. [VO(IV)] = 0.25mM and [L] = 1mM.

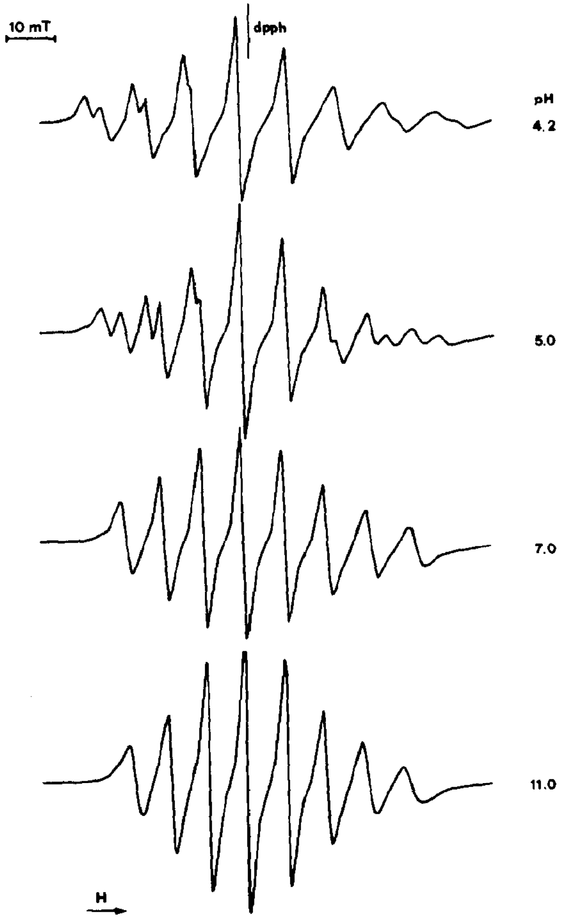

Fig. 2. Room-temperature e.p.r. spectra of VO^{2+}–D-galacturonic acid solutions (ligand-to-metal molar ratio, 2) as a function of pH.

the considerable variation of the donor set involved in the VO^{2+} coordination. The deprotonation of the (12-2) complex is explained by dissociation followed by coordination of the second hydroxyl function (replacing carboxylate), *i.e.*, the formation of two chelate rings involving four deprotonated hydroxyl groups. In the (12-4) complex, the two ligands are most likely bound by C(3)–O^- and C(4)–O^-.

D-Glucuronic acid (LH) has a dissociation constant (pK_1 3.07; *cf.* 3.28 for D-galacturonic acid), which corresponds to the carboxyl group. This value is similar to that reported earlier[4]. The experimental data indicate that complex formation with the VO^{2+} ion begins at pH 3–4. At pH >5, the e.p.r. spectra broaden and vanish (Fig. 4), suggesting the formation of polymeric species. The metal remains in the form of oxovanadium(IV) ion and is bound to sugar molecules. The c.d.

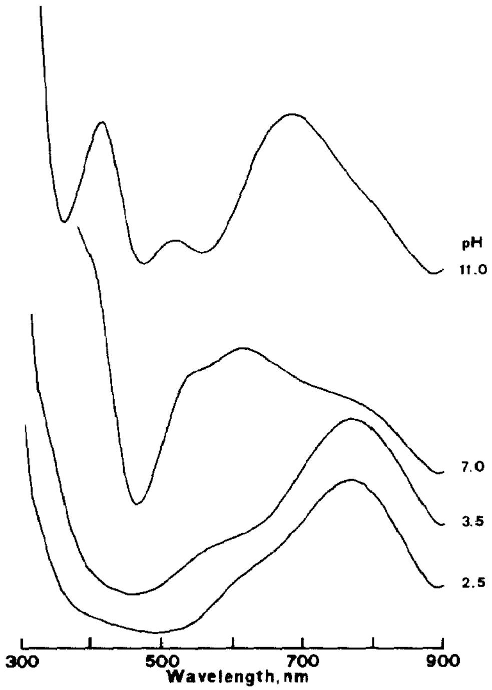

Fig. 3. Electronic spectra of VO^{2+}–D-galacturonic acid solutions (ligand-to-metal molar ratio, 4) as a function of pH.

spectra show that the Cotton effects of the *d–d* transitions of this polymeric species are centered at wavelengths similar to those observed for the complexes with D-galacturonic acid (Table IV), although with much lower intensities. The assumption of a dinuclear complex only[12] does not allow a reliable fitting of the potentiometric data, and only the stability constant for the monomeric (120) complex was evaluated (Table III). According to the e.p.r. spectra, a monomeric species reappears at pH >9 (Fig. 4) and its parameters are very close to that of the (12-4) complex with D-galacturonic acid (Table IV). Thus, the coordination mode in each of these complexes is the same, *i.e.*, through four deprotonated hydroxyl functions. This suggestion is supported by the electronic and c.d. spectra (Table IV and Fig. 5).

The different coordinating behaviour of the sugar ligands must reflect the difference in structure at C-4. According to e.p.r. spectra, the monodentate coordination of each ligand *via* carboxylate seems to be similar. The major differences are observed when the coordination of the first deprotonated hydroxyl group occurs. This behaviour strongly suggests that, for D-galacturonic acid, HO-4 is involved in the metal ion (O^-, COO^-) chelation, whereas this type of coordination is sterically less favourable for D-glucuronic acid. Therefore, the (O^-, COO^-) chelates are not formed by the latter ligand, and increase of pH leads to the forma-

TABLE IV

SPECTROSCOPIC PARAMETERS FOR OXOVANADIUM(IV) COMPLEXES

Species	*E.p.r.*		*Absorption* [λ(*nm*), (ε)][c]	*C.d.*[a] [λ(*nm*), (Δε)][c]
	g_o	A_o[b]		
D-*Galacturonic acid*				
(12-1)	1.970	97	630(9)sh	550(+0.065)
			770(18)	>700(−0.15)
(12-2)	1.975	82	550(9)sh	
			610(30)	607(−0.153)
			760(23)sh	
(12-4)	1.975	78	415(26)	403(−0.383)
			520(12)	518(+0.285)
			680(27)	618(−0.848)
D-*Glucuronic acid*				
(120)	1.967	96	570(12)sh	
			760(18)	
Polymeric species			550(16)	418(+0.020)
			790(18)	520(−0.029)
				650(+0.061)
(12-4)	1.976	77	420(25)	418(+0.183)
			510(11)	525(−0.117)
			690(29)	623(+0.030)

[a] *d–d* Transitions from B_2 to E_2, B_1 and A_1, respectively. [b] 10^{-4} cm^{-1}. [c] ε and Δε are calculated for the total oxovanadium(IV) concentration and are given in M^{-1}.cm^{-1}.

tion of polynuclear species. The deprotonation of the second hydroxyl group allows the restoration of a ligand coordination mode similar to that of D-galacturonic acid, *i.e.*, the formation of a complex in which four ionised hydroxyl groups from two ligand molecules chelate the metal ion.

The copper(II) complexes with D-galacturonic and D-glucuronic acids are considerably weaker than those of oxovanadium(IV) and they have been studied[4–7,13]. Although the involvement of the carboxyl group in metal ion binding is accepted generally, the second coordination centre is controversial. Makridou *et al.*[4] assumed only monodentate ("acetate like") complexation of D-galacturonic acid, whereas Aruga[13], besides the carboxyl binding, proposed also outer-sphere electrostatic interaction of the metal ion with the endocyclic sugar oxygen. Kohn and Hirsch[5] concluded that HO-4 of D-galacturonic acid is involved, together with the carboxyl group, in metal ion coordination. Ternai *et al.*[6] concluded that complexation of D-glucuronic acid is pH dependent and, at pH >4.5, cupric ions are chelated through the carboxyl group and HO-C3. The above results for oxovanadium(IV) complexes indicate that the involvement of HO-4 in the metal ion chelation is sterically less favourable. The stability constants obtained earlier are incomplete and are presented in Table V.

Polarography at pH <6 indicates the formation of two Cu(II) complexes with

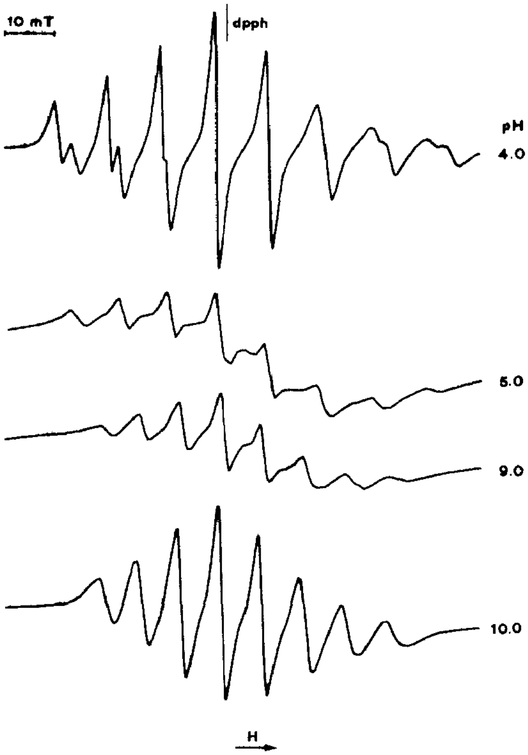

Fig. 4. Room-temperature e.p.r. spectra of VO^{2+}–D-glucuronic acid solutions (ligand-to-metal molar ratio, 2) as a function of pH.

TABLE V

STABILITY CONSTANTS OBTAINED FOR COPPER(II) COMPLEXES WITH D-GLUCURONIC ACID AND D-GALACTURONIC ACID FROM POLAROGRAPHIC DATA

Ion	*GlcA*	*GalA*	*Ref.*
H^+	2.95	3.17	4
	3.07	3.28	This work[a]
Cu^{2+}	1.48 (110)	1.81 (110)	4
	1.01 (110) 4.1 (120)		1[b]
	1.44 (110) 2.47 (120)	1.80 (110) 3.10 (120)	This work[c]

[a] See Table III. [b] See text. [c] From polarographic data according to the De Ford–Hume method[14], using data from Tables I and II.

each ligand (Table V). The stability constants obtained with the De Ford–Hume method[14] are in reasonable agreement with the potentiometric data of Makridou *et al.*[4] as far as equimolar complexes are concerned. However, CuL_2 species were not reported by these authors. The data of Payne and Magee[1] concerning the complexes with D-glucuronic acid appear to involve incorrect calculations.

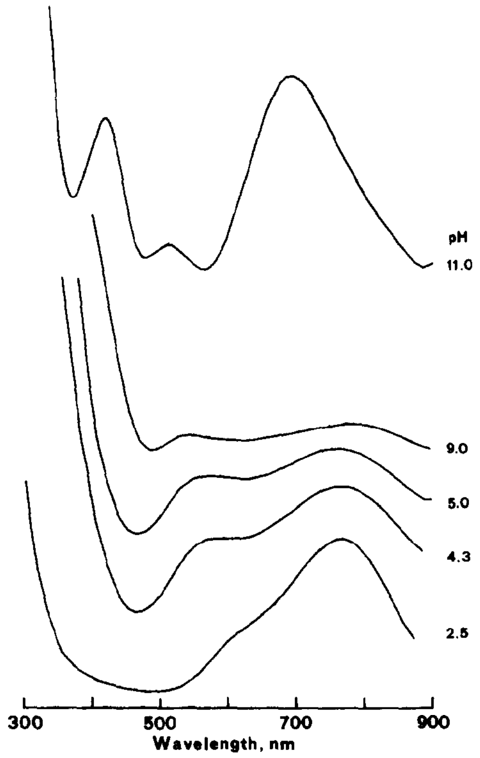

Fig. 5. Electronic spectra of VO^{2+}–D-glucuronic acid solutions (ligand-to-metal ratio, 4) as a function of pH.

Because of the low stability of the cupric complexes with each sugar acid, potentiometric titrations over a wide pH range were possible only at high ligand-to-metal ratios. Therefore, the accuracy of the calculated stability constants may be significantly lower than for the oxovanadium(IV) complexes (Table III). However, they indicate the formation of complexes which are similar to, but considerably weaker than, those of oxovanadium(IV) and D-galacturonic acid. The formation of precipitates in the Cu(II)–D-glucuronic acid system did not allow potentiometric titrations to be performed in a wide pH range. The good agreement between the stability constants obtained from the polarographic and potentiometric data for the (120) complex with D-galacturonic acid (Tables III and V) suggests, however, that the data presented in Table III for the Cu(II) complexes are reasonably close to the real values. The (110) species is substantiated only by the polarographic measurements and, due to its low concentration, is not indicated by the potentiometric data computer calculations (see refs. 15 and 16).

The e.p.r. spectra show the formation of several complexes in the Cu(II)–D-galacturonic acid solutions. The parameters presented in Table VI fit very well the model proposed by the potentiometric data given in Table III. The coordination

TABLE VI

E.P.R. PARAMETERS FOR THE COPPER(II) COMPLEXES WITH D-GALACTURONIC ACID AND D-GLUCURONIC ACID, AND ASSIGNMENT OF COORDINATION MODES

Proposed coordination	$g_{\parallel}$	$A_{\parallel}{}^{a}$
D-*Galacturonic acid*		
2 {COO^-} (120)	2.383	142
2 {COO^-, O^-} (12-2)	2.323	173
2 {O^-, O^-} (12-4)	2.293	178
D-*Glucuronic acid*		
2 {COO^-} (120)	2.383	142
2 {COO^-, O^-} (12-2)	2.324	174
2 {O^-, O^-} (12-4)	2.287	185

[a] 10^{-4} cm^{-1}.

modes in the corresponding species are identical to those proposed for the VO^{2+} complexes and they are given in Table VI. The variation of the spectral parameters follows well the species distribution plot obtained from the potentiometric titrations.

ACKNOWLEDGMENTS

This work was supported by the Polish Ministry of National Education (Project RP.II.13.1.5) and the Consiglio Nazionale delle Ricerche (Rome).

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