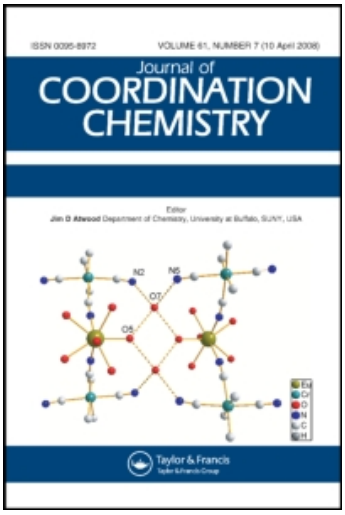

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Organomercury(II) Complexes of Kojic Acid

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NOTE

ORGANOMERCURY(II) COMPLEXES OF KOJIC ACID

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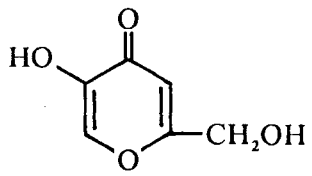
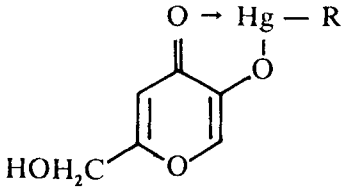
Key words: mercury(II), kojic acid, complexes, bacteriostats, synthesis

Kojic acid or 5-hydroxy-2-(hydroxymethyl)pyran-4-one (I) is an antibiotic substance produced by *Aspergilli.* It is known to inhibit the growth of *E. coli* and *S. aureus.*[1,2] Since the antibiotic activity of a drug is altered in the presence of metal ions, it was thought worthwhile to synthesise and characterise a few organomercury (II) complexes of kojic acid of the type RHgL(II) [R = C_6H_5, *o*-, *p*-HOC_6H_4, *p*-$AcOC_6H_4$, 2-C_4H_3O (2-furyl); HL = kojic acid] and to study their activity against *E. coli* and *P. pyocyanea* bacterial strains. This is a sequel to our investigation of metal ion-biomolecule interaction.[3-6].



(I)



(II)

EXPERIMENTAL

An Elico CM-82 conductivity bridge was used for conductance measurements. IR spectra were recorded on a Perkin Elmer 621 grating spectrometer, while UV spectra were recorded on a Perkin Elmer 554 spectrometer. A Jeol FX spectrometer was used for measuring ^1H and ^{13}C NMR spectra. Nitrobenzene was purified for conductance measurements by the method of Fay *et al.*[7] C_6H_5HgCl[8], *o*-, *p*-HOC_6H_4HgCl[9], *p*-$AcOC_6H_4HgCl$[10] and 2-C_4HgCl[11] were prepared by standard methods. Kojic acid was purchased from Fluka AG, Switzerland. The complexes were prepared by stirring a solution of RHgCl (0.01 mol) and kojic acid (0.01 mol) in 50 cm^3 THF. After about 3h, the contents were filtered, the filtrate was evaporated under vacuum to one fourth of its volume and petroleum ether was added. The complexes precipitated and were recrystallised from acetone.

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TABLE I
Physical Characteristics and Analytical Data for the Complexes

Complex	Dec. temp. 0°C	Λ^a (C=1.5 x 10^{-3}M)	Found (calc.) %		
			Hg	C	H
C_6H_5HgL	188	0.50	47.85(47.97)	34.32(34.37)	2.38(2.34)
o-HOC_6H_4HgL	110	0.46	46.14(46.21)	33.16(33.10)	2.26(2.30)
p-HOC_6H_4HgL	188	0.48	46.18(46.21)	33.14(33.10)	2.33(2.30)
p-$AcOC_6H_4HgL$	180	0.50	42.01(42.14)	35.29(35.22)	2.58(2.52)
2-C_4H_3OHgL	120	0.52	49.25(49.11)	29.26(29.34)	2.02(1.96)

[a]In ohm^{-1} cm^{-2} mol^{-1}

RESULTS AND DISCUSSION

Satisfactory elemental analyses and spectral studies reveal that the complexes are of good purity. The complexes are white in colour and soluble in THF, DMSO and acetone. Conductance measurements in nitrobenzene solution (10^{-3}M) are of the order of 0.50 ohm^{-1} cm^2 mol^{-1}, indicating that the complexes are non-electrolytes. This data is summarized in Table I.

According to Katritzky and Jones[12] the absorption at 1665 cm^{-1} in kojic acid is assigned to the ν(C=O) stretching frequency. This is lower than the conventional carbonyl stretching frequency partly because of intramolecular hydrogen bonding and partly the weakening of the C=O bond by contributions from resonance structures. On complexation, this frequency is further lowered by about 50 cm^{-1} indicating that the C=O group bonds to Hg the ν(C=C) stretching frequency observed at 1580 cm^{-1} in the ligand is shifted to about 1560 cm^{-1} in complexes.[13]

In kojic acid, the band due to phenolic OH stretching[14] occurs at 3200 cm^{-1} and that due to δ(OH)[13] at 1300 cm^{-1}. These bands are absent in the spectra of the complexes, indicating the presence of appropriate metal-oxygen bonds. The ν(OH) of the $-CH_2OH$ group is observed at about 3550 cm^{-1}. A weak absorption around 450 cm^{-1} is attributed to ν(Hg-O) stretching vibrations.[15] The bands at 1290 and about 1220 cm^{-1} in case of the ligand and complexes respectively are due to C-O-C stretching.[14]

The electronic spectrum of kojic acid shows a band at 255 nm (log ε 4.8) due to the π-π^* transition of the carbonyl group. In the metal complexes this band is shifted to about 272 nm (log α 3.8).* The shift is also attributed to the involvement of this group in complexation.

In ^{1}H nmr spectra, the following signals are attributed to the presence of kojic acid in the complexes: δ 2.56 (s, 2H, CH_2 at C_2); δ 6.93 (s, 1H, H_3); δ 8.05 (s, 1H, H_6). In free kojic acid, the signal due to H_3 absorbs at δ 6.45 and that due to H_6 at δ 7.80. The downfield shift in these signals is attributed to the involvement of carbonyl at C_4 and hydroxyl at C_5 in complexation.

In the ^{13}C nmr spectra of kojic acid the signals due to C_4 and C_5 appear at 174.61 and 145.82 ppm respectively.[16] In the case of the complexes, the former signal is shifted to about 179.52 ppm and the latter to about 148.71 ppm indicating also that complexation involves the above mentioned donors. The CH_2OH resonance occurs at about 59.6 ppm. The data are given in Table II.

The metal complexes were tested against *E. coli* and *P. pyocyanea* bacterial strains using kojic acid as the standard for comparing activity. The samples were screened at

*ε in units of M^{-1} cm^{-1}.

TABLE II
^{13}C Nmr Data for the Complexes.†

Complex	R						Kojic acid				
	C_1	C_2	C_3	C_4	C_5	C_6	C'_2	C'_3	C'_4	C'_g	C'_h
C_6H_5HgL	150	135.8	128	127.5	128	135.8	168.6	109.8	179.5	148.7	140
o-HOC_6H_4HgL	138.5	161.7	120	132.2	122.2	140.4	168.5	109.8	179.5	148.8	139.8
p-HOC_6H_4HgL	147.3	150.9	135.6	156.5	135.6	150.9	168.6	109.9	179.4	148.7	139.8
p-$AcOC_6H_4$	148.8	138.2	122.1	150.8	122.1	138.2	168.7	109.8	179.5	148.7	139.7

†In ppm.

two concentrations, 25 $\mu g\ cm^{-1}$ and 50 $\mu g\ cm^{-1}$. Although the complexes were equally active against both bacterial strains, their inhibitory power was greater than that of the control. The compounds showed greater inhibition at the higher concentration. The p-$AcOC_6H_4HgL$ and p-HOC_6H_4HgL complexes were found to have higher activity than the others.

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