

## LETTERS TO THE EDITOR

### SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH MEPAZINE HYDROCHLORIDE

MEPAZINE hydrochloride, MH, 10-[(1-methyl-3-piperidyl) methyl] pterothiazine hydrochloride is recommended as a new reagent for the spectrophotometric determination of osmium(VIII). The method involves the formation of a red coloured species which is believed to be a radical cation in 1.0–3.0 N HCl. For full development of colour intensity a ten-fold molar excess of the reagent is required. The red species exhibits maximum absorbance at 512–516 nm. The reagent and the metal do not absorb at this wavelength. The maximum colour development takes place after 8 minutes and the absorbance readings remain constant for one hour at 10–50°C. No change in absorbance is observed when the order of addition of reactants was varied. Beer's law is valid over the concentration range 0.16–6.4 ppm and the optimum range as evaluated by Ringbom's method<sup>1,2</sup> is 1.0–6.2 ppm. According to Sandell's expression, the sensitivity of the reaction is 0.018 µg/cm<sup>2</sup> and the molar absorptivity is  $1.05 \times 10^4$  litre mol<sup>-1</sup> cm<sup>-1</sup> at 515 nm.

Sample solutions containing 4 µg/ml of osmium prepared by the standard procedure gave a relative error of  $\pm 0.7\%$  and standard deviation of 0.002. The following amounts (µg/ml) of diverse ions are found to give less than  $\pm 2\%$  error in the determination of 4 µg/ml of osmium(VIII): rhodium(III) 15, iridium(III) 14, platinum(IV) 2, ruthenium(III) 0.6, palladium(II) 0.6, iron(III) 2, cobalt(II) 72, nickel(II) 660, copper(II) 70, fluoride 1460, chloride 4500, bromide 1900, iodide 3, nitrate 1575, phosphate 1420, sulphate 6000, acetate 7340, oxalate 920 and EDTA 5800.

Synthetic mixtures corresponding to osmiridium alloy were prepared and the osmium content was determined following the standard procedure. The results are given in Table I. The proposed method offers the advantages of simplicity, rapidity and good sensitivity without the need for heating or extraction.

**Standard procedure.**—To an aliquot of the sample solution containing 4 to 160 µg of osmium(VIII) (prepared from osmium tetroxide in 0.2 M sodium hydroxide and standardized iodimetrically<sup>3</sup>) were added 8.5 ml of 6N HCl and 2 ml of 0.2% aqueous MH solution and the volume was made up to 25 ml by adding doubly distilled water. The solution was mixed well and the absorbance was measured at 515 nm after standing 8 minutes against a reagent blank prepared similarly.

TABLE I  
*Determination of osmium in synthetic mixtures corresponding to osmiridium alloy*

Os(VIII) taken, ppm	Ir(III) added, ppm	Os(VIII) found*, ppm
1.20	0.3	1.20
2.40	0.6	2.39
3.60	0.9	3.59
4.80	1.2	4.79
6.00	1.5	5.99

\* The amount of osmium (VIII) found is based on ten determinations.

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### THERMODYNAMIC FUNCTIONS OF SOME BIVALENT METAL ION CHELATES OF DL-α-AMINO BUTYRIC ACID

#### Introduction

In previous publications<sup>1-3</sup> from this laboratory, the stability constants of some amino-acid metal chelates, including those formed with α-amino-butyric acid have been reported. It is recognised that for a proper understanding of chelation reactions, a knowledge of the thermodynamic functions is imperative. Gergely *et al.*<sup>4</sup> have earlier reported thermodynamic functions of some common bivalent transition metal chelates of α-aminobutyric acid. In the present paper we report the thermodynamic functions ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) of Be(II), Cd(II) and Hg(II) chelates of DL-α-aminobutyric acid. Their formation has been potentiometrically studied by Irving and Rossotti's<sup>5</sup> method.

*Experimental*

Three mixtures (acid), (acid + ligand) and (acid + ligand + metal ion) were potentiometrically titrated separately with 0.1 M NaOH solution in a double walled titration vessel with a sealed on water jacket at a fixed temperature. Total volume was kept at 50 ml each time and the ionic strength of 0.1 M was maintained by adding NaClO<sub>4</sub> solution. Purified nitrogen was bubbled both before and during the titration to exclude CO<sub>2</sub>. pH measurements were done by a Leeds-Northrup pH-meter using glass electrode. From the shifts in the pH titration curves, the values of  $\bar{n}_A$ ,  $\bar{n}$  and  $pL$  were calculated by Irving and Rossotti's<sup>5</sup> method.

*Results and Discussion*

The protonation constants as well as metal-ligand stability constants, as computed by correction term and successive approximation methods, at different temperatures, are given in Table I.

The enthalpy change ( $\Delta H$ ) has been determined by temperature coefficient method by the equation :

$$\Delta H = 2.303 RT_1 T_2 (\log K_2 - \log K_1) / (T_2 - T_1)$$

and the free energy and entropy changes were calculated as :

$$\Delta G = -2.303 RT \log K$$

and

$$\Delta G = \Delta H - T \Delta S.$$

The results are reported in Table II.

It is observed that the stability constants show a regular decrease with the increase in temperature.

A perusal of thermodynamic functions shows that Be(II) chelates have a very favourable enthalpy change for the formation of first chelated complex whereas Hg(II) chelates are more entropy stabilized. The entropy change for the second step in Be(II) system is rather anomalous.

TABLE I

*Stability constants of Be, Cd and Hg chelates of DL- $\alpha$ -aminobutyric acid at different temperatures ( $\mu = 0.1$  M NaClO<sub>4</sub>).*

Metal ion		Stability constants				
		20° C	25° C	30° C	35° C	40° C
Be(II)	Log K <sub>1</sub> H	9.62 ± 0.02	9.49 ± 0.02	9.35 ± 0.03	9.22 ± 0.02	9.07 ± 0.03
	Log K <sub>2</sub> H	2.35 ± 0.01	2.30 ± 0.02	2.26 ± 0.02	2.23 ± 0.01	2.20 ± 0.01
	Log K <sub>1</sub>	6.90 ± 0.02	6.80 ± 0.03	6.71 ± 0.02	6.61 ± 0.02	6.52 ± 0.03
	Log K <sub>2</sub>	5.95 ± 0.02	5.90 ± 0.01	5.86 ± 0.01	5.82 ± 0.01	5.77 ± 0.02
	Log $\beta_2$	12.85 ± 0.04	12.70 ± 0.04	12.57 ± 0.03	12.43 ± 0.03	12.29 ± 0.05
Cd(II)	Log K <sub>1</sub>	3.49 ± 0.01	3.46 ± 0.02	3.42 ± 0.01	3.39 ± 0.01	3.35 ± 0.02
	Log K <sub>2</sub>	3.44 ± 0.01	3.40 ± 0.02	3.35 ± 0.02	3.31 ± 0.02	3.27 ± 0.02
	Log $\beta_2$	6.93 ± 0.02	6.86 ± 0.04	6.77 ± 0.03	6.70 ± 0.03	6.62 ± 0.04
Hg(II)	Log K <sub>1</sub>	6.61 ± 0.03	6.55 ± 0.02	6.50 ± 0.01	6.46 ± 0.02	6.41 ± 0.02
	Log K <sub>2</sub>	5.51 ± 0.02	5.47 ± 0.02	5.44 ± 0.01	5.41 ± 0.01	5.38 ± 0.01
	Log $\beta_2$	12.12 ± 0.05	12.02 ± 0.04	11.94 ± 0.02	11.87 ± 0.03	11.79 ± 0.03

TABLE II

*Thermodynamic functions of Be, Cd and Hg chelates of DL- $\alpha$ -aminobutyric acid (Temp. 20° C,  $\mu = 0.1$  M NaClO<sub>4</sub>)*

Metal ion	$-\Delta G_1$ Kcal/mole	$-\Delta G_2$ Kcal/mole	$-\Delta H_1$ Kcal/mole	$-\Delta H_2$ Kcal/mole	$\Delta S_1$ e.u.	$\Delta S_2$ e.u.
Be(II)	9.28 ± 0.04	8.05 ± 0.01	7.7 ± 0.1	3.7 ± 0.1	5 ± 1	15 ± 1
Cd(II)	4.72 ± 0.03	4.64 ± 0.03	3.1 ± 0.1	3.4 ± 0.1	5 ± 1	5 ± 1
Hg(II)	8.94 ± 0.03	7.46 ± 0.03	4.5 ± 0.1	2.8 ± 0.1	15 ± 1	16 ± 1



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## SYNTHESIS OF KANZAKIFLAVONE-1 AND KANZAKIFLAVONE-2

MUNEHISA ARISAWA *et al.*<sup>1,2</sup> have recently isolated kanzakiflavone-1 (I) and kanzakiflavone-2 (II) from *Iris unguicularis* POIR and assigned to them, the structures 5, 8-dihydroxy-4'-methoxy-6, 7-methylenedioxyflavone and 5, 4'-dihydroxy-6, 7-methylenedioxyflavone respectively on the basis of spectral and chemical studies. In order to confirm the above structures, we have synthesised I and II which are identical with the natural compounds in all respects.

For the synthesis of kanzakiflavone-2 (II), a mixture of scutellarein<sup>3</sup> (III) (500 mg), methylene iodide (0.4 ml), dry acetone (100 ml) and ignited  $K_2CO_3$  (2 g) was refluxed for 18 hrs. The mixture was filtered and the solvent distilled. Water was added to the residue and the yellow solid which separated was filtered. It was purified by passing over a column of silica gel and crystallised from alcohol as yellow prisms (200 mg), m.p. 311-312° (lit.<sup>2</sup> m.p. 310°).

UV:  $\lambda_{max}^{MeOH}$  284, 334 nm (log  $\epsilon$  4.12, 4.32)

$\lambda_{max}^{MeOH} + AlCl_3$  : 290 (sh), 295, 360 nm (log  $\epsilon$  4.10, 4.19, 4.32).

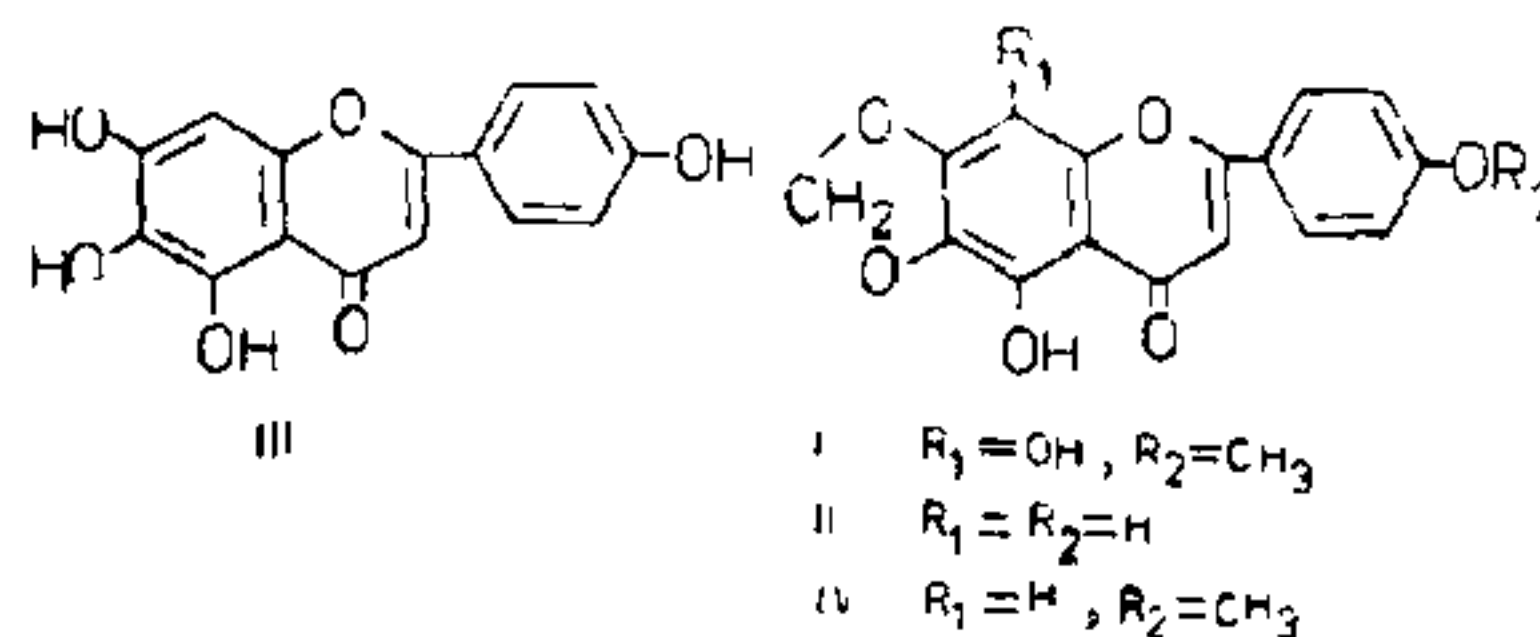
IR:  $\nu_{max}^{nujol}$  3300, 1680, 1030, 930  $cm^{-1}$

NMR ( $CDCl_3$ ,  $\delta$ ) 7.65 (d,  $J = 9.0$  Hz, 2H at  $C_2$ , and  $C_6$ , positions),

6.82 (d,  $J = 9.0$  Hz, 2H at  $C_3$ , and  $C_5$ , positions),

6.50 (s, 1H,  $C_8H$ ), 6.30 (s, 1H,  $C_7H$ ), 6.00 (s, 2H,  $O-CH_2-O$ ).

The spectral data of this compound were found to be in full agreement with the data given in literature<sup>2</sup> for (II).



For the synthesis of Kanzakiflavone-1 (I), (II) (300 mg) was partially methylated with dimethyl sulphate (0.14 g), dry acetone (5 ml) and  $K_2CO_3$  (2.0 g) by refluxing for 6 hrs. On working up in the usual way, it gave the methyl ether (IV) which crystallised from  $CH_3OH$  as pale yellow needles (200 mg), m.p. 250-252°.

UV:  $\lambda_{max}^{MeOH}$  280, 330 nm (log  $\epsilon$  4.10, 4.30)

IR:  $\nu_{max}^{nujol}$  1680  $cm^{-1}$  (carbonyl)

NMR: ( $CDCl_3$ ,  $\delta$ ) 7.65 (d,  $J = 9.0$  Hz, 2H at  $C_2$ , and  $C_6$ , positions),  
6.82 (d,  $J = 9.0$  Hz, 2H at  $C_3$ , and  $C_5$ , positions),  
6.50 (s, 1H,  $C_8H$ ), 6.30 (s, 1H,  $C_7H$ ),  
6.00 (s, 2H,  $-O-CH_2-O-$ ), 3.80 (s, 3H,  $OCH_3$ ).

The methyl ether (IV) (200 mg) was dissolved in aqueous KOH (10 ml, 5%) and pyridine (5 ml) added. The solution was stirred at 15-20° and  $K_2S_2O_8$  solution (500 mg in 40 ml of  $H_2O$ ) added dropwise during the course of four hours. The solution was left overnight and acidified with dil. HCl to Congo red. The precipitated unreacted compound was filtered and the filtrate extracted with ethyl acetate to ensure complete removal of the unreacted compound. The aqueous layer was treated with conc. HCl (6 ml) and  $Na_2SO_3$  (100 mg) and heated on water bath (70°) for 30 min. when a brown mass separated. It was filtered and crystallised from pyridine-methanol as yellow needles (60 mg), m.p. 291-293° (lit.<sup>1</sup> m.p. 291-293°).

UV:  $\lambda_{max}^{MeOH}$  280, 345 nm (log  $\epsilon$  4.11, 4.30)

$\lambda_{max}^{MeOH} + AlCl_3$  295, 370 nm (log  $\epsilon$  4.10, 4.28)

IR:  $\nu_{max}^{nujol}$  3340, 1680, 1030, 930, 770  $cm^{-1}$

NMR: ( $CDCl_3$ ,  $\delta$ ) 7.80 (d,  $J = 9.0$  Hz, 2H at  $C_2$ , and  $C_6$ , positions),

6.80 (d,  $J = 9.0$  Hz, 2H at  $C_3$ , and  $C_5$ , positions),

6.42 (s, 1H,  $C_8H$ ), 5.96 (s, 2H,  $O-CH_2-O$ ),  
3.82 (s, 3H,  $OCH_3$ ).

The spectral data of this compound were found to be in full agreement with the literature<sup>1</sup> data of kanzakiflavone 1 (I).

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