

coleoptile. Of the lignans tested, eudesmin had little effect on the inhibition of germination of the seed and seedling growth.

TABLE I  
Effect of lignans on germination of peanut, cucumber and rice

Compound used	Concentration ppm	Germination percentage		
		Peanut	Cucumber	Rice
Control	..	75	98	85
Fargesin	50	08	06	80
	100	06	02	68
	200	02	00	60
Sesamin	50	28	83	86
	100	20	80	82
	200	12	72	83
Eudesmin	50	62	88	87
	100	48	84	84
	200	30	76	84

Taylorson and Hendricks<sup>4</sup> observed that applied compounds can be effective on germination of seeds by stimulating hormone action on membranes or on the inhibition of specific enzymes or as components of respiratory chain. The mode of action of the previously recognised compounds having inhibitory effect is still inexplicable. Van Sumere *et al.*<sup>5</sup> made an attempt to understand the possible regulatory role of naturally occurring coumarins and phenolics. Valentin Kefeli<sup>6</sup> attributed growth inhibitory property to phenolic products. Leucoanthocyanins from *Aesculus* fruits were reported to have growth promoting ability.

In our study, the furofuranoid lignans (Fig. 1) having piperonyl residue, *viz.*, fargesin (I) and sesamin (II) showed considerable retardation in the germination of peanut and cucumber. Only fargesin showed some effect on rice. Eudesmin (III), which has got only veratryl residues but not methylenedioxy group, showed little inhibition. From these data it may be inferred that the piperonyl residue plays a role in growth inhibition. It is also evident from the data that the inhibitory effect of fargesin and sesamin on the germination of lipid storing seeds is more pronounced than in the seeds containing carbohydrates as storage product. It appears that the effect is on the end product initiating enzymes controlling lipid mobilization.

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#### ELECTROMETRIC AND THERMODYNAMIC STUDIES ON THE RARE-EARTH CHELATES OF 2-( $\alpha$ -2-OXOPENTYLIDENEIMINO) ETHANE SULPHONIC ACID SCHIFF BASE

No work appears to have been done<sup>1-3</sup> on the chelates of 2-( $\alpha$ -2-oxopentylideneimino) ethane sulphonic acid ( $H_2OE$ ) with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III).

The apparatus and reagents employed were the same as reported earlier<sup>4</sup>.  $H_2OE$  was synthesised from acetyl acetone and taurine by the general procedure referred earlier<sup>5</sup>, m.p. 142°, it gave satisfactory elemental analysis.

The stability constants of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III)-chelates with  $H_2OE$  were determined by Calvin-Bjerrum pH-titration technique as used by Irving and Rossotti<sup>6</sup>. For the evaluation of the thermodynamic stability constants, experiments were carried out in media of low ionic strengths (0.1, 0.05, 0.01 M  $NaClO_4$ ) at 25°, 35° and 45°.  $H_2OE$  was titrated in the absence and in the presence of the metal ions of interest with 0.1 M NaOH solution and the titration curves had the usual shapes.

The dissociation constants ( $\log K_1^H$  and  $\log K_2^H$ ) of  $H_2OE$  and stability constants ( $\log K_1$  and  $\log K_2$ ) of its rare-earth chelates are shown in Table I.

From Table I it is apparent that stability of the rare-earth chelates enhance with rise of temperature

TABLE I

*Dissociation constants of H<sub>2</sub>OE and stability constants of its rare-earth chelates at 0.1M NaClO<sub>4</sub>*

Ligand/Metal chelates	log K <sub>1</sub> <sup>H</sup> /log K <sub>1</sub>			log K <sub>2</sub> <sup>H</sup> /log K <sub>2</sub>		
	25°	35°	45°	25°	35°	45°
H <sub>2</sub> OE	10.20	9.90	9.60	8.60	8.30	8.05
La(III)	5.75	6.05	6.22	4.08	4.80	4.95
Ce(III)	6.30	6.40	6.50	4.40	4.95	5.10
Pr(III)	6.60	6.70	6.80	4.95	5.30	5.40
Nd(III)	6.85	6.95	7.05	5.45	5.50	5.55
Sm(III)	7.05	7.12	7.22	5.67	5.78	5.88
Gd(III)	7.30	7.40	7.47	5.87	5.95	6.05
Tb(III)	7.60	7.65	7.75	6.10	6.20	6.30
Dy(III)	7.80	7.90	7.97	6.35	6.47	6.55
Ho(III)	8.05	8.15	8.25	6.60	6.65	6.73

TABLE II

*Average stability constants, thermodynamic parameters and magnetic moments of rare-earth chelates of H<sub>2</sub>OE*

Metal chelate	log K°			-ΔG K. cal/ mole 25°	ΔH K. cal/ mole 35°	ΔS deg/cal/ mole 35°	μ <sub>eff</sub> B.M. 308° K
	25°	35°	45°				
La(III)	10.40	11.30	11.80	13.41	29.05	142.70	Diamagnetic
Ce(III)	11.20	11.80	12.20	14.59	19.51	114.50	2.25
Pr(III)	12.15	12.60	12.90	15.71	14.09	100.10	3.39
Nd(III)	13.00	13.20	13.40	16.77	6.50	78.20	3.68
Sm(III)	13.25	13.50	13.70	17.34	7.80	84.46	1.42
Gd(III)	13.70	13.80	13.95	17.95	7.58	85.76	7.86
Tb(III)	14.30	14.50	14.70	18.67	7.58	88.20	9.54
Dy(III)	14.80	15.00	15.20	19.29	8.02	91.77	10.40
Ho(III)	15.30	15.50	15.70	19.97	7.15	91.16	10.44

and atomic number. Thus, the stabilities of the metal chelates follow the order La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) which is in agreement with the findings of Stagg and Powell<sup>2</sup>. The thermodynamic stability constants have been obtained by extrapolation of the experimentally obtained constants to zero ionic strengths and their values along with other related parameters have been summarised in Table II.

The values of the overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been evaluated using the Gibb's-Helmholtz equation (Table II). The ΔG of the chelates have more negative values at 45° than at 25° and 35°. The ΔH values are positive suggesting that some steric strain exists

around the metal ion in the chelates due to fused rings. The ΔS values are also positive.

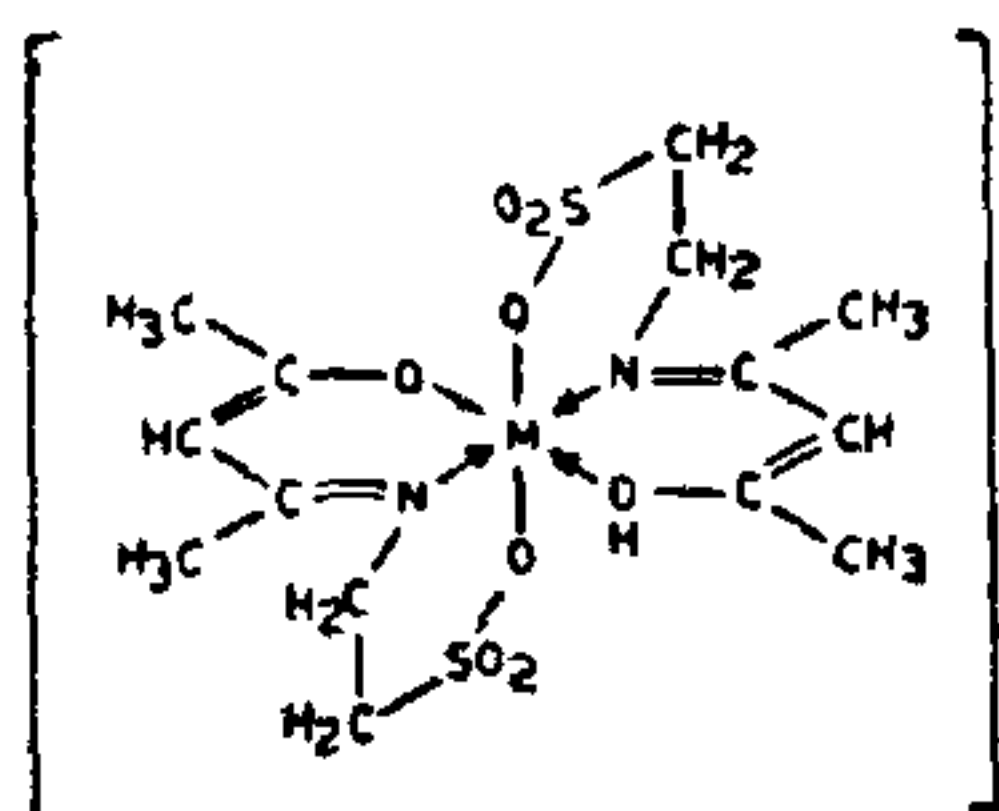
The data were analysed in term of Harned's relation<sup>3</sup> and the plot of (pK<sub>m</sub><sup>H</sup>-ct<sup>2</sup>) versus *t* was found linear. The values of 0° and pK<sub>m</sub><sup>H</sup> for H<sub>2</sub>OE were found to be 418.3 and 9.45 respectively. ΔH values calculated from Harned's and Gibb's-Helmholtz equations have been found similar.

These chelates were isolated in the solid state by the procedure already reported<sup>9</sup>. The metal chelates were analysed and found to possess 1:2 metal-ligand stoichiometry. These compounds do not possess sharp m.p. but decompose on heating between 255°-290° C. Excepting the lanthanum chelate which was found diamagnetic, all the compounds were found



paramagnetic (Table II). From the magnetic moments which are very close of spin, only values it is apparent that in these compounds there is no metal-metal bonding and hence no spin-exchange occurs and they exist as monomer.

In the I.R. spectra of  $H_2OE$  three bands were observed at  $1090\text{ cm}^{-1}$ ,  $1610\text{ cm}^{-1}$  and  $3500\text{ cm}^{-1}$  assignable to  $\nu SO_3H$ ,  $\nu C=N$  and  $\nu OH$  respectively. In the metal chelates the band at  $1090\text{ cm}^{-1}$  disappeared suggesting coordination through sulphonate group.  $\nu C=N$  of  $H_2OE$  around  $1610\text{ cm}^{-1}$  was shifted to lower frequency on chelation indicating the participation of azo-methine nitrogen in coordination. Two more bands in the narrow ranges of  $530\text{--}520\text{ cm}^{-1}$  and  $440\text{--}410\text{ cm}^{-1}$  reflect M-O and M-N bonds in the metal chelates which may have the octahedral stereochemistry as shown in Fig. 1.



where  $M(III) = \text{La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, OR Ho}$ .

FIG. 1. Rare-earth chelates of 2-( $\alpha$ -2-oxopentylideneimino) ethane sulphonic acid.

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## SEED-BORNE INFECTION OF RICE BY *PYRICULARIA ORYZAE* IN KARNATAKA

THE rice disease caused by *Pyricularia oryzae* Cav. is one of the worst diseases of rice in Karnataka. The disease is said to be seed borne<sup>1-5</sup>. Kapoor and Singh<sup>6</sup> reported failure to demonstrate the seed borne nature of the pathogen. Studies were therefore undertaken to know the seed borne nature of infection of this pathogen.

Seed samples were collected from the Regional Research Station, Mandya, Karnataka, during December 1978 and stored at room temperature. Testing of the seed samples was done by Blotter method.

The seeds were sown on three layers of moistened blotters placed in Petri dishes at the rate of 25 seeds per dish. The dishes were incubated at  $24 \pm 2^\circ\text{C}$  under alternating cycles of 12 h near fluorescent tubes (40 cm from the top) and darkness.

Out of fifty seed samples tested, only twelve seed samples showed the infection of *Pyricularia oryzae* (2-52%). The *P. oryzae* produced effuse growth of greyish mycelium with conidiophores arising singly or in groups, covering a part of the seed near hilum region. Conidiophores are slender, straight, greyish or pale brown, smooth, bearing clusters of conidia which are typically obpyriform or obclavate, hyaline, 2 septate,  $20.0\text{--}27.0 \times 8.0\text{--}10.0\ \mu$ .

Neergaard<sup>7</sup> stated that blast of rice *P. oryzae* is frequently seed-borne in all rice producing countries. The blotter method used in this investigation was employed earlier by Neergaard and Saad<sup>8</sup>. The seed-borne infection of *P. oryzae* is definitely established in the present investigation.

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