

PAR is one of the most sensitive reagent for determination of vanadium. Reagent also absorbs strongly at the wavelength of maximum absorption. It is quite selective in presence of DCTA. However, even in presence of DCTA, uranium, niobium, titanium and zirconium interfere. Complete colour development requires 30 min. and complex is stable for 2 hr only. Xylenol orange is also a sensitive reagent; however molybdenum and tungsten interferes seriously. The reagent 5, 7-dihydro-8-quinolinol is quite sensitive and also selective. The colour is extractable into chloroform but starts fading immediately. Strict control of acidity is required to extract the complex into *n*-heptyl alcohol and procedure is quite lengthy.

In the present method DPQH does not absorb at all at λ_{\max} 550 nm which is an advantage since water reference can also be used. Furthermore determination can be carried out even in the presence of large amounts of molybdenum, tungsten, thorium, tantalum and moderate amount of titanium.

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OCCURRENCE OF THE RARE ALKALOID MARITIDINE IN *ZEPHYRANTHES ROBUSTA* AND *Z. SULPHUREA*

THE plant members of Amaryllidaceae are known to possess poisonous and medicinal properties¹. *Zephyranthes robusta*² and *Z. sulphurea*³ were examined chemically and the alkaloids tazettine, haemanthamine, lycorine and a new alkaloid m.p. 262–64° were reported. Further work was carried out on the above alkaloid (m.p. 262–64°) and it was identified as maritidine.

The bulbs of *Z. robusta* and *Z. sulphurea* obtained from a nursery in Sikkim were examined separately. The bulbs were extracted with alcohol and concentrated to a small bulk adding water towards the end. This aqueous suspension was adjusted to pH 6 and extracted with ether and chloroform. The remaining aqueous suspension was then made alkaline (pH 8) and extracted with chloroform (A).

Z. robusta: The extract A on crystallization directly gave lycorine (Fraction I) m.p. 255–57°, $[\alpha]_D^{30} = -100^\circ$ (alcohol), $C_{16}H_{17}NO_4$; acetate m.p. 216°. The mother liquor was subjected to chromatography on alumina when two crystalline fractions were obtained (Fractions II and III). Fraction II was identified as haemanthamine m.p. 201–03°, $[\alpha]_D^{30} = +37.5^\circ$ (chloroform), $C_{17}H_{19}NO_4$; picrate m.p. 220°. Fraction III was obtained from chloroform eluates, m.p. 260–62°. It answered tests for alkaloids and analysed for $C_{17}H_{21}NO_3$.

Z. sulphurea: The extract A on direct crystallization gave stout prisms (Fraction IV). The mother liquor on chromatography gave Fraction V in benzene-chloroform eluates and Fraction VI in chloroform eluates. Fraction IV, tazettine, m.p. 204°, $[\alpha]_D^{30} = 166^\circ$ (chloroform), $C_{18}H_{21}NO_5$; hydrochloride m.p. 218°. Fraction V, haemanthamine, m.p. 203°. $[\alpha]_D^{30} = 33.5^\circ$ (chloroform), $C_{17}H_{19}NO_4$; picrate m.p. 222°. Fraction VI, stout prisms from methanol, m.p. 262–64°. The compound was soluble in methanol and almost insoluble in chloroform. It answered all tests for alkaloids. $[\alpha]_D^{30} = +28^\circ$ (methanol), Found: C, 71.54; H, 7.20; N, 4.95%. $C_{17}H_{21}NO_3$ (287.4) requires C, 7.43; H, 7.33; N, 5.06%. I.R. ν_{\max} (KBr) 3610, 3020, 2820, 1270, 1120, 1100, 1080, 740 cm^{-1} . Picrate m.p. 192–94°; oxidation with manganese dioxide gave an α, β -unsaturated ketone, m.p. 140–43°. Fractions III and VI possessed same properties and were identical in TLC and I.R. This alkaloid was found to have similar properties as those of the new alkaloid (alkaloid 16) reported by Sandberg and Michel⁴ from *Pancreatum maritimum*. Wildman⁵ elucidated the constitution of the alkaloid 16 in an unpublished work and named it maritidine at the same time of our isolation of this new alkaloid from *Zephyranthes* species. Thus the above alkaloid isolated was identified as maritidine and further confirmation of the identity was obtained by m.m.p., TLC and I.R. comparison with authentic maritidine.

Maritidine is the first alkaloid with 5, 10 *b* ethanophenanthridine nucleus containing dimethoxy rather than methylenedioxy substituents at C-8, C-9.

This is the second report of isolation of the rare alkaloid maritidine from Amaryllidaceae and first report from *Zephyranthes* genera.

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**PHYSICOCHEMICAL INVESTIGATION
OF RARE-EARTH CHELATES OF
2-(N-2-HYDROXY BENZYLIDINEIMINO)
ETHANE SULPHONIC ACID**

A PERUSAL of the literature¹⁻² has revealed that no work has been done on the rare-earth chelates of 2-(N-2-hydroxy benzylideneimino) ethane sulphonic acid (H₂BE). The physicochemical investigation of the rare-earth-H₂BE chelates have been carried out using potentiometric, magnetic and spectral techniques.

2-(N-2-hydroxybenzylideneimino) ethane sulphonic acid (H₂BE) was synthesised from salicylaldehyde and taurine by the procedure already reported³.

Potentiometric titrations of mixtures containing (A) perchloric acid alone, (B) perchloric acid and the ligand (H₂BE) and (C) perchloric acid, ligand and metal-ion solution have been carried out by the method of Irving and Rossotti⁴.

Mean values of dissociation constants (log K₁^H and log K₂^H) as obtained by the method of interpolation at half \bar{n} values⁵ and interpolation at various \bar{n} values method, have been found to be 10.05 and 8.35 at 25°, 9.81 and 8.09 at 35°, and 9.67 and 7.84 at 45°, respectively. The formation curves for the metal-ligand system attain maxima at $\bar{n} > 1.5$ which indicate that 1:1 and 1:2 chelates are formed. The stability values of the metal chelates were refined by various computational methods⁶. The values obtained by different methods were found in agreement and their average values are summarised in Table I. Thus the stability of the chelates increases with decreasing ionic size of the metal ions, *i.e.*, La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III). The values of the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of the metal chelates have also been included in Table I.

TABLE I

Molecular weight, average stability, thermodynamic parameters and magnetic moments of rare-earth chelates of H₂BE

Metal chelates	Mol. wt. Calc. (Found)	Stability constants log K ₁ log K ₂	- ΔG K. cal/mole	ΔH K. cal/mole at 35°	ΔS Cal/deg/mole	μ_{eff} B.M. 308°
[LaL ₂]	579 (561)	5.65 (5.74) 6.79* 4.50 (4.55) 4.60*	14.07 (14.51) 16.57*	21.50	116.7	diamagnetic
[CeL ₂]	580 (565)	6.05 (6.77) 7.18* 4.63 (5.00) 5.05*	14.72 (16.59) 17.76*	25.52	136.8	2.28
[PrL ₂]	581 (567)	6.59 (7.16) 7.50* 4.73 (5.28) 5.30*	15.62 (17.54) 18.56*	23.84	134.4	3.37
[NdL ₂]	584 (572)	7.06 (7.42) 7.94* 4.99 (5.65) 5.75*	16.63 (18.42) 19.92*	27.35	148.6	3.66
[SmL ₂]	590 (580)	7.62 (7.83) 8.02* 5.26 (5.75) 5.81*	17.77 (19.14) 20.13*	20.60	129.0	1.45
[GdL ₂]	597 (582)	8.03 (8.13) 8.61* 5.79 (6.24) 6.29*	14.06 (20.25) 21.68*	21.52	136.2	7.84
[TbL ₂]	598 (579)	8.39 (8.42) 8.88* 6.05 (6.62) 6.80*	19.92 (21.19) 22.80*	17.49	125.9	9.51
[DyL ₂]	602 (592)	8.51 (8.65) 9.29* 6.40 (6.94) 7.07*	20.57 (22.98) 23.81*	14.95	119.9	10.43
[HoL ₂]	605 (595)	8.80 (8.93) 9.54* 7.00 (7.28) 7.40*	21.80 (22.85) 24.65*	19.02	135.9	10.42

The values in parenthesis are at 35° and those with asterisk mark are at 45° C; and L₂ — C₂₈H₂₉N₃O₅S₂.