

ing two sugars is yet to be established. Full details will be published in due course.

The authors thank CSIR, New Delhi, for the award of a fellowship to GVSR.

June 10, 1980.

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### RARE FLAVONE GLUCURONIDES FROM *MENTHA SPICATA*

A. G. RAMACHANDRAN NAIR AND R. GUNASEGARAN  
Jawaharlal Institute, Pondicherry 605 006, India

IN continuation of the earlier isolation of diosmin and diosmetin-7-glucoside from the leaves of *Mentha spicata*<sup>1</sup> (family: Labiatae) we report below the additional occurrence of two rare flavone glucuronides—diosmetin-7-0-glucuronide and luteolin-3'-0-glucuronide.

Fresh leaves of *M. spicata* were processed in the usual way<sup>1</sup> and the aqueous concentrate after the removal of diosmin was extracted with ethyl methyl ketone and concentrated to yield a mixture of two flavone derivatives. They were separated by column chromatography over cellulose using BAW solvent for developing; the elution being followed by UV fluorescence and PC. The compound which was eluted first crystallised from MeOH-Me<sub>2</sub>CO as light yellow needles, m.p. 212-13°,  $[\alpha]_D^{25} - 89^\circ$  (C<sub>6</sub>H<sub>5</sub>N). It was purple under UV and UV/NH<sub>3</sub>, had  $\lambda_{max}$  241sh, 253, 268 and 345 nm (MeOH as well as NaOAc) and yielded diosmetin and D-glucuronic acid (1:1) on acid and enzyme ( $\beta$ -glucuronidase) hydrolysis. It was identified as diosmetin-7-0- $\beta$ -D-glucuronide and the identity confirmed by comparison

including co-PC with an authentic sample<sup>2</sup>. The second compound was crystallised from MeOH to yield yellow needles, m.p. 220-21°,  $[\alpha]_D^{25} - 96.5^\circ$ . It was purple under UV changing to yellow with NH<sub>3</sub>, had  $\lambda_{max}$  260, 270, 285sh, 338 (MeOH); 275, 328, 395 (NaOMe); 270, 390 (NaOAc); 260, 265, 345 (NaOAc/H<sub>3</sub>BO<sub>3</sub>) and 270, 290sh, 340, 390 (AlCl<sub>3</sub> and AlCl<sub>3</sub>/HCl) and yielded luteolin and D-glucuronic acid (1:1) on acid and enzyme hydrolysis. It had R<sub>f</sub>: (X100, Whatman 1, 28° C) 52 (H<sub>2</sub>O), 5 (5% HOAc), 14 (15% HOAc), 55 (50% HOAc), 61 (BAW), 46 (phenol), 63 (Forestal) and 52 (*t*-BAW). The flavonoid was identified as luteolin-3'-0- $\beta$ -D-glucuronide and the identity confirmed by direct comparison with an authentic sample<sup>3</sup>.

Our results show the occurrence of two rare flavone glucuronides in *M. spicata*, the isolation of luteolin-3'-0-glucuronide being the first from a higher plant.

Our thanks are due to Dr. K. R. Markham, D.S.I.R., Petone, New Zealand, for part of the spectral data and direct comparison of our compound with luteolin-3' glucuronide; to U.G.C., New Delhi, for financial assistance and the Director of our Institute for encouragement.

July 21, 1980.

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### SPECTRAL AND MAGNETIC STUDIES OF LANTHANON CHELATES OF SOME SCHIFF BASES

C. P. GUPTA, K. G. SHARMA AND R. K. MEHTA  
Department of Chemistry, University of Jodhpur  
Jodhpur 342 001, India

A LARGE number of the rare-earth chelates of tridentate Schiff bases have been synthesised and studied in these laboratories<sup>1,2</sup>. No studies have been made on Pr(III), Nd(III) and Sm(III) chelates of 3-(3-hydroxy-2-naphthylideneiminino)propanoic acid (H<sub>3</sub>NP) and N-acetylacetone-isovaleric acid (H<sub>3</sub>AI). The present paper describes the spectral and magnetic properties of these chelates.

The ligands H<sub>3</sub>NP and H<sub>3</sub>AI and their lanthanon chelates were prepared by the method reported earlier<sup>3</sup>. The apparatus and reagents used were the same as referred earlier<sup>3</sup>.

The results of elemental analyses, conductance and magnetic studies are included in Table I.

### Results and Discussion

These compounds gave satisfactory elemental analysis and are soluble in dioxane and DMF. Their molecular weights were determined by Gallenkamp semimicro ebulliometer using dioxane as solvent. Analytical results (Table I) show their 1:2 (metal-ligand) stoichiometry. These compounds behave as non-electrolytes as revealed by their very low molar conductance (Table I) in dioxane.

From the magnetic moments, it is apparent that in these compounds there is no metal-metal bonding and no spin-exchange occurs and hence they exist as monomers. These values also suggest that orbital contribution is almost quenched by the crystalline field.

**Electronic Spectra**—The electronic spectra of the compounds in dioxane have been analysed to find out the use of nephelauxetic effect in the case of these materials. The nephelauxetic parameter ( $\beta$ ) as determined by the method of Jorgensen *et al.*<sup>4,5</sup> was used for calculating the ( $\beta$ ) values for these transitions. It is observed during the present investigation that there

TABLE I  
Yield, colour, molecular weight, magnetic moment and conductance data of  $H_2NP$  and  $H_2Al$ -rare-earth chelates

Compound	Yield %	Colour	Mol. Wt. Found (Calcd.)	Decomposition temp. °C	$\mu_{eff}$ B.M. 308°K	Conductance ohm <sup>-1</sup> mole <sup>-1</sup> cm <sup>2</sup>
[PrL <sub>2</sub> ]	69	Creamish	609 (624)	325	3.33	7.8
[NdL <sub>2</sub> ]	79	Light orange	615 (627)	310	3.64	9.5
[SmL <sub>2</sub> ]	77	Off-white	621 (633)	280	1.46	6.0
[PrL <sub>2</sub> ']	71	Pale yellow	519 (535)	305	3.39	5.5
[NdL <sub>2</sub> ']	68	Yellow	525 (538)	295	3.68	8.2
[SmL <sub>2</sub> ']	74	Gray	530 (544)	315	1.42	7.1

Where L=(H<sub>2</sub>NP) and L'=(H<sub>2</sub>Al).

TABLE II  
Electronic spectral data and related bonding parameters of  $H_2NP$  and  $H_2Al$  chelates

Ion	H <sub>2</sub> NP chelates in DMSO band in cm <sup>-1</sup>	H <sub>2</sub> Al chelates in DMSO band in cm <sup>-1</sup>	J levels	$(1-\beta) \times 10^{-2}$		$\delta$ (%)		$b^4 \times 10^{-1}$	
				H <sub>2</sub> NP chelates	H <sub>2</sub> Al chelates	H <sub>2</sub> NP chelates	H <sub>2</sub> Al chelates	H <sub>2</sub> NP chelates	H <sub>2</sub> Al chelates
Pr(III)	22290	22390	<sup>3</sup> H <sub>4</sub> → <sup>3</sup> P <sub>2</sub>	0.75	0.31	0.7557	0.3109	0.06	0.03
	21110	21160	→ <sup>3</sup> P <sub>1</sub>	1.03	0.79	1.0407	0.7963	0.07	0.06
	20660	20640	→ <sup>3</sup> P <sub>0</sub>	0.77	0.57	0.7760	0.5733	0.06	0.05
	16810	16920	→ <sup>1</sup> D <sub>2</sub>	1.23	0.58	1.2454	0.5834	0.08	0.05
Nd(III)	19470	19490	<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> H <sub>9/2</sub>	0.30	0.20	0.3093	0.2004	0.03	0.03
	18850	18950	→ <sup>4</sup> F <sub>7/2</sub> , <sup>4</sup> S <sub>3/2</sub>	1.39	0.78	1.4084	0.7862	0.08	0.06
	17210	17250	→ <sup>4</sup> F <sub>9/2</sub>	0.63	0.40	0.6340	0.4014	0.05	0.04
	14530	14530	→ <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> G <sub>7/2</sub> *	0.75	0.75	0.7994	0.7994	0.06	0.06
	13360	13350	→ <sup>4</sup> G <sub>7/2</sub>	1.12	0.74	1.1224	0.7455	0.07	0.06
	12420	12480	→ <sup>4</sup> G <sub>9/2</sub>	0.95	0.47	0.9795	0.4986	0.07	0.04
Sm(III)	24760	24760	<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> F <sub>9/2</sub>	0.40	0.40	0.4025	0.4025	0.03	0.03
	23700	23750	→ <sup>6</sup> P <sub>5/2</sub>	0.59	0.37	0.5945	0.3714	0.05	0.04
	21500	21540	→ <sup>4</sup> I <sub>13/2</sub>	0.60	0.41	0.6006	0.4217	0.05	0.04

\* Red shift.

is shift in band positions towards the lower wave number relative to the aquo complexes. It may, therefore, be concluded that 4f-orbitals of rare-earth ions do not participate in bonding. The bands observed in the case of Pr(III), Nd(III) and Sm(III) chelates may be due to transitions from ground level  $^3H_4$ ,  $^4I_{9/2}$  and  $^6H_{5/2}$  to the excited J levels of 4f<sup>n</sup> configuration, respectively. The present data also show that the nephelauxetic values for different J levels vary considerably. This is in agreement with the findings of Rastogi *et al*<sup>6</sup>. The  $(1 - \beta)$  values can be used to estimate a parameter of bonding, known as Sinha's covalency parameter<sup>7</sup> ( $\delta$ ). Another bonding parameter  $b^{1/2}$  given by Henrie and Choppin<sup>8</sup> has also been calculated, which measures the amount of 4f ligand mixing. The values of  $(1 - \beta)$ ,  $\delta$  and  $b^{1/2}$  are included in Table II.

The positive values for  $(1 - \beta)$  and  $\delta$ -parameters in these complexes suggest that the bonding between metal and ligand is covalent as compared to that in metal-aquo ion. All average values of  $\delta$ -parameter for H<sub>2</sub>NP and H<sub>2</sub>AI complexes are, however, positive but smaller than unity in the case of H<sub>2</sub>AI complexes. It indicates weak covalent bonding in H<sub>2</sub>AI complexes than in H<sub>2</sub>NP complexes.  $b^{1/2}$  values (Table II) are higher for H<sub>2</sub>NP complexes than for H<sub>2</sub>AI complexes which indicate relatively more covalent bonding in H<sub>2</sub>NP complexes than in H<sub>2</sub>AI complexes.

The absorption spectra of Nd(III) complex solution in DMSO show an appreciable red shift with respect

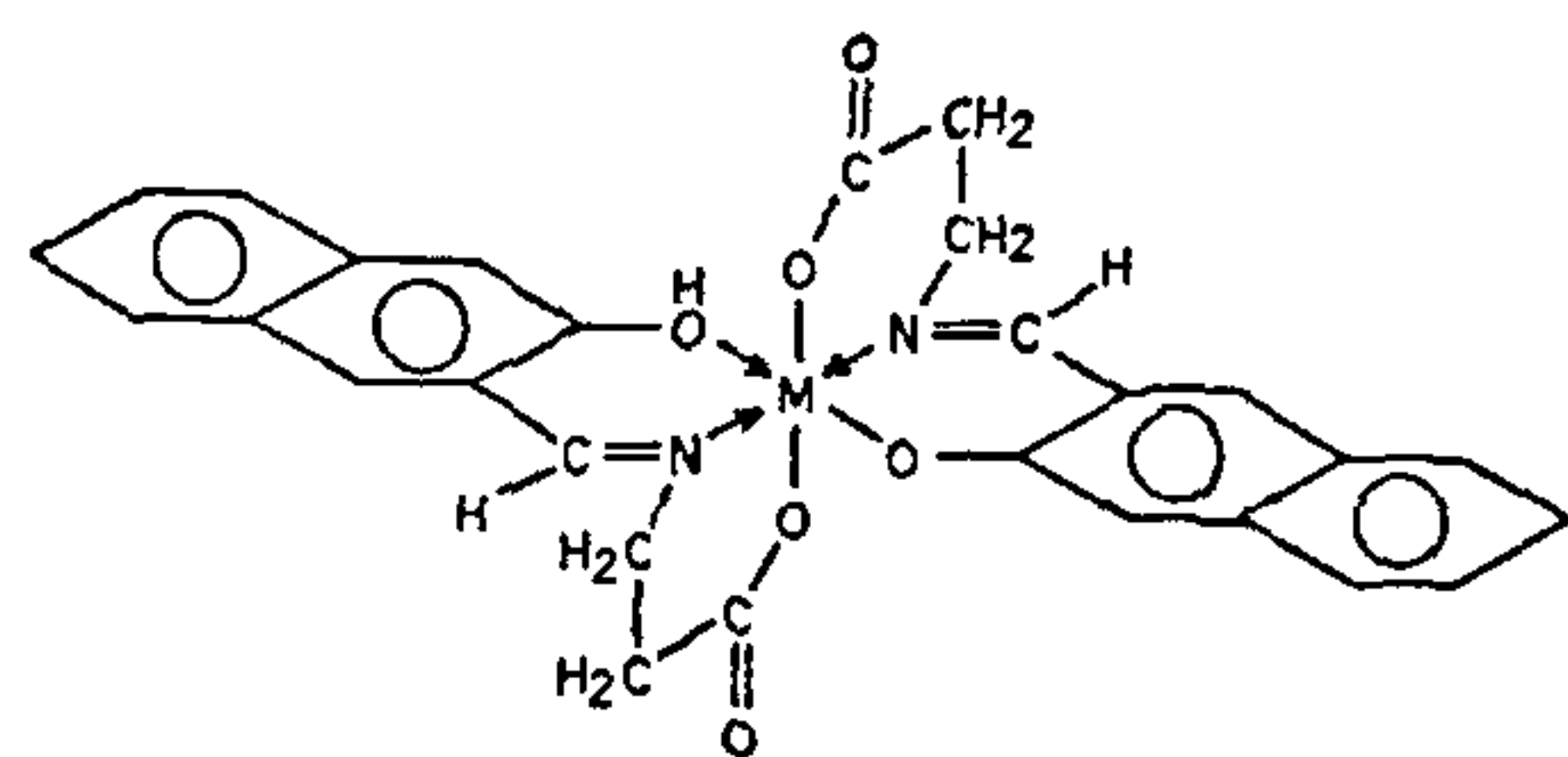
to aquo-cation involving  $^4I_{9/2} \rightarrow ^2G_{7/2}$ ,  $^4G_{5/2}$  transitions, respectively.

In the i.r. spectra of the ligands five bands are observed at 3370 cm<sup>-1</sup>, 2580 cm<sup>-1</sup>, 1690 cm<sup>-1</sup>, 1610 cm<sup>-1</sup> and 1590 cm<sup>-1</sup>, for H<sub>2</sub>NP and 3390 cm<sup>-1</sup>, 2590 cm<sup>-1</sup>, 1695 cm<sup>-1</sup>, 1640 cm<sup>-1</sup> and 1605 cm<sup>-1</sup> for H<sub>2</sub>AI which correspond to  $\nu$ OH,  $\nu$ COOH,  $\nu$ C=O,  $\nu$ C=N and naphthalene ring [H<sub>2</sub>NP];  $\nu$ OH,  $\nu$ COOH,  $\nu$ C=O,  $\nu$ C=C and  $\nu$ C=N [H<sub>2</sub>AI], respectively. In the metal chelates the  $\nu$ C=N has lowered from 1610 cm<sup>-1</sup> and 1605 cm<sup>-1</sup> to 1560–1580 cm<sup>-1</sup> indicating involvement of azomethine nitrogen in complexation. The  $\nu$ OH in the metal chelates has also lowered from 3370 cm<sup>-1</sup> and 3390 cm<sup>-1</sup> to 3330–3350 cm<sup>-1</sup> and 3350–3370 cm<sup>-1</sup>. The  $\nu$ C=O has also lowered from 1690 cm<sup>-1</sup> and 1695 cm<sup>-1</sup> to 1665–1685 cm<sup>-1</sup> indicating coordination through carboxylate group. Appearance of bands in the narrow ranges 410–415 and 405–425 cm<sup>-1</sup> suggest metal-nitrogen bondings in the chelates. Formation of (M-O) bonds due to the deprotonation of carboxylic group of the H<sub>2</sub>NP and H<sub>2</sub>AI is evidenced by the appearance of bands in the ranges 500–525 cm<sup>-1</sup> and 505–520 cm<sup>-1</sup> respectively. In the case of H<sub>2</sub>NP chelates the band at 1590 cm<sup>-1</sup> may be attributed to the presence of naphthalene ring<sup>9</sup>.

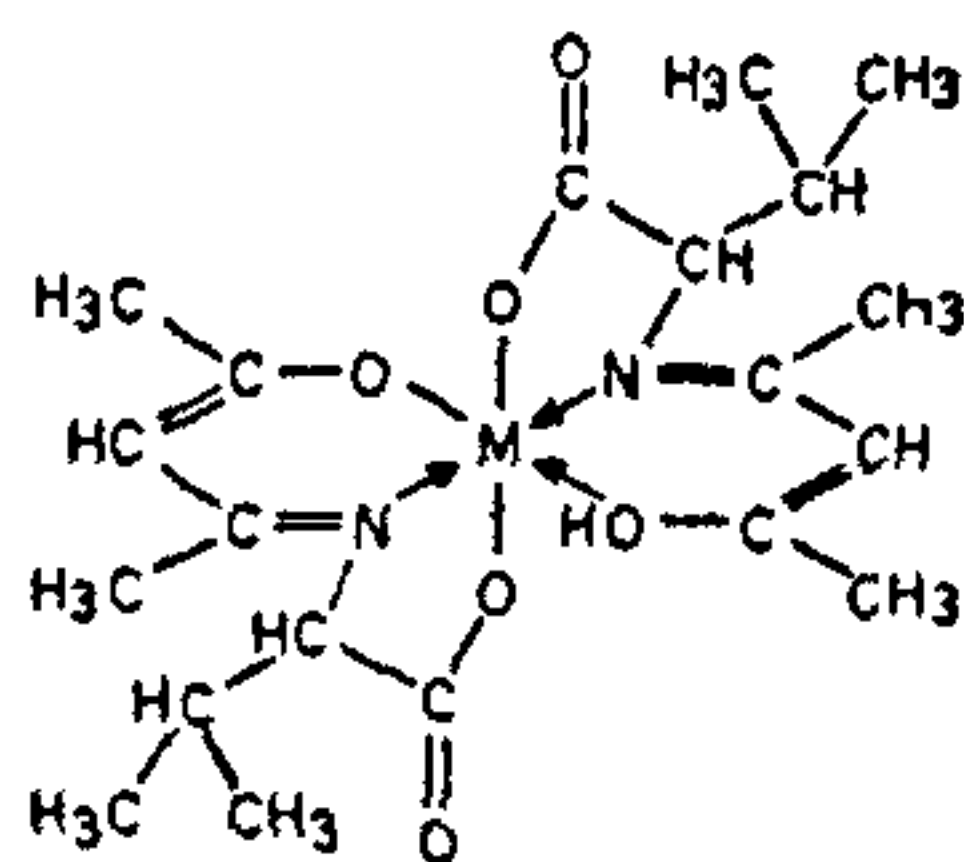
Based on the above evidences an octahedral stereochemistry may be assigned to these compounds as shown in Fig. 1.

Authors are grateful to C.S.I.R., New Delhi, for the award of Post-Doctoral and Senior Fellowships to two of them (JPG and KGS).

August 5, 1980.



H<sub>2</sub>NP - CHELATE



H<sub>2</sub>AI - CHELATE

Where M = Pr(III), Nd(III) & Sm(III).

FIG. 1. Lanthanum chelates of H<sub>2</sub>NP and H<sub>2</sub>AI.

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