

dispersions. The bands from 2918 Å to 2838 Å appear sharp, single-headed and exhibit certain features which may be due to isotopic effect. From 2838 to 2813 Å, they do not possess sharp bands and below 2813 Å, they are in pairs with constant separation. All the attempts to assign these bands as diatomic emitter failed.

Intense band-heads of C-X system of transient HgBr are observed on 21' concave grating spectrograph in II order (table 1). The calculated ( $P_{\text{head}} - Q_{\text{head}}$ ) separation and isotopic-shifts (Hg<sup>81</sup>Br-Hg<sup>79</sup>Br) were obtained to account for these observed sub-band-heads separations for ascribing the bands to diatomic emitter. It is evident from the table that the observed band-head separations do not match with the above two calculations. This leads us to conclude that these bands are not due to diatomic HgBr. The emitter of these bands is definitely triatomic HgBr<sub>2</sub> as all the sub-band-heads, appearing with each main strong band, have been successfully explained with the present assignments in table 1, which gives the symmetric, bending and antisymmetric stretch frequencies for the upper and lower states of triatomic HgBr<sub>2</sub> emitter. The vibronic splitting of (012-212), (110-230), (100-120), (111-011) and (112-012) bands on 35' grating confirms the present assignment of the bands as triatomic emitter.

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### COORDINATION POLYMERS OF COBALT(II), NICKEL(II), COPPER(II), ZINC(II) AND CADMIUM(II) WITH 3-ALLYL-1-(2-MERCAPTO-4-OXO-3(4H)-QUINAZOLINYL)-2-THIOPSEUDOUREA

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COBALT(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes with 3-allyl-1-(2-mercapto-4-oxo-3(4H)-quinazolinyl)-2-thiopseudourea (H<sub>2</sub>L) have been synthesized and characterized on the basis of analytical, thermal, conductance, magnetic and spectral (IR, NMR, ESR and electronic) data. The data indicate the formation of ligand bridged polymeric octahedral complexes in which the ligand behaves as a pentadentate biprotic ligand. The sixth coordination position has been occupied by the water molecule.

The complex formation with 2-mercaptoquinazolin-4(3H)-one (figure 1) takes place through the nitrogen atom at position 1 and sulphur atom of the mercaptan group<sup>1</sup>. There are reports of oxygen also taking part in coordination<sup>2</sup>. Extensive work has been done in the field of metal complexes with its 3-substituted alkyl/aryl derivatives. The studies with potentially donor group at position 3 have not received much attention. The present communication reports the coordination polymers of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) with 3-allyl-1-(2-mercapto-4-oxo-3(4H)-quinazolinyl)-2-thiopseudourea (H<sub>2</sub>L).

3-Allyl-1-(2-mercapto-4-oxo-3(4H)-quinazolinyl)-2-thiopseudourea (H<sub>2</sub>L) was prepared by heating a mixture of allylthiocyanate (0.60 g) and 3-amino-2-mercaptoquinazolin-4(3H)-one<sup>3</sup> (1 g) on a steam bath for 2 hr. The solid mass was triturated with ethanol (2 ml) and collected under suction. It was crystallized from ethanol. M. P. 210°C. Characterization data: Found S = 21.81, N = 19.26; calculated for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>OS<sub>2</sub> S = 21.92, N = 19.18.

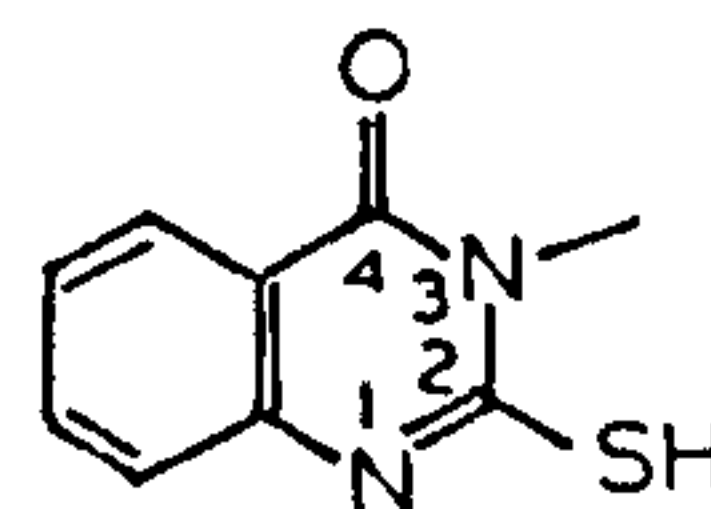


Figure 1.

Table 1 Analytical and conductance data

Complexes	colour	Found (calculated)%				H <sub>2</sub> O*	ΛM mhos cm <sup>2</sup> mol <sup>-1</sup>
		M	N	S			
CoL(H <sub>2</sub> O)	Light pink	16.13 (16.06)	15.18 (15.26)	17.54 (17.44)	4.98 (4.90)	6	
NiL(H <sub>2</sub> O)	Sea green	16.18 (16.11)	15.34 (15.27)	17.52 (17.45)	4.83 (4.90)	5	
CuL(H <sub>2</sub> O)	Light green	17.18 (17.10)	15.13 (15.07)	17.15 (17.23)	4.75 (4.84)	8	
ZnL(H <sub>2</sub> O)	Dirty White	17.62 (17.51)	15.09 (15.00)	17.24 (17.14)	4.90 (4.82)	7	
CdL(H <sub>2</sub> O)	Light Yellow	26.83 (26.74)	13.24 (13.32)	15.38 (15.22)	4.34 (4.28)	10	

\*TGA data; H<sub>2</sub>L = C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>OS<sub>2</sub>.

The ethanolic solution of H<sub>2</sub>L (1 mmol) was treated with hot aqueous solution of the metal acetate (1 mmol). The pH of the reaction mixture was maintained at 3.5–5.0 with the help of acetate buffer and then refluxed for 2–3 hr. The product separated out on stirring and cooling the reaction mixture, was filtered, washed with ethanol and dried in vacuo over CaCl<sub>2</sub>. Hydrogen gas was bubbled during the preparation of cobalt(II) complex.

The complexes were analysed for sulphur by gravimetric method and nitrogen by Kjeldahl's method. Metals were estimated by the standard procedure. The molar conductance, thermal analyses, magnetic susceptibility and infrared data were estimated as reported earlier<sup>4</sup>. The electronic spectra were recorded on a spectrophotometer (Karlzessis USP-2p). The <sup>1</sup>H NMR spectra were recorded in deuterated DMF (Varian EM 360) at 60 Hz using TMS as the external standard. The ESR spectrum of the Cu(II) complex was recorded at room temperature on a Varian E-4 X-band spectrophotometer.

The complexes are powdery in appearance, insoluble in water and common organic solvents and are moderately soluble in nitromethane, DMF and DMSO. This indicates that the complexes could be polymeric. The low values of conductance (table 1) measured in DMF at 1 × 10<sup>-3</sup> M indicate that the complexes are non-ionic. The results of elemental analyses (table 1) indicate 1:1 (metal-ligand) composition. The TGA studies reveal that the weight loss up to 260–320°C (table 1) corresponds to one water molecule suggesting a general formula ML(H<sub>2</sub>O). The complete decomposition takes place at 680–740°C leaving behind the metal oxides as

residue. The endothermic peak observed at 260–320°C in the DTA thermograms of the complexes suggest the presence of coordinated water molecule. The complexes show the thermal stability in the order Cd(320°C) > Zn(310°C) > Ni(290°C) > Cu(280°C) > Co(260°C).

The infrared spectrum of the ligand exhibit bands at 3320, 3220 and 3080 cm<sup>-1</sup> assignable to μ<sub>NH</sub> mode. A single and broad band in this region was observed in the complexes. It is, therefore, difficult to draw any definite conclusion regarding the involvement of NH group in bonding. However, the band due to δ<sub>NH</sub> deformation at 1600 cm<sup>-1</sup> in the ligand remains almost unaffected in the complexes. The band at 1720 cm<sup>-1</sup> in the ligand is attributed to ν<sub>C=O</sub> mode and shifts by 20–35 cm<sup>-1</sup> towards the lower frequency region in the complexes indicating the participation of oxygen atom in coordination. The ν<sub>C=N</sub> band at 1660 cm<sup>-1</sup> in the ligand suffers a reduction by 10–25 cm<sup>-1</sup> in the complexes suggesting the bonding through the nitrogen atom of C = N group. The band at 2630 cm<sup>-1</sup> in the ligand is attributed to ν<sub>S-H</sub> vibration. This band is absent in the complexes suggesting deprotonation of the thiolic SH group. The band at 790 cm<sup>-1</sup> in the ligand, which is assigned to ν<sub>C-S</sub> mode, has been lowered to 760–750 cm<sup>-1</sup> in the complexes showing that the sulphur atom is involved in coordination. The rocking and wagging modes of vibration for water molecule at 860 and 650 cm<sup>-1</sup> respectively in the complexes indicate coordinated nature of the attached water molecule<sup>5</sup>. The ν<sub>O-H</sub> band of the coordinated water molecule appears around 3620 cm<sup>-1</sup> in the complexes. The ligand and the

Table 2 Electronic spectral data and ligand field parameters

Complexes	'max cm <sup>-1</sup>	Assignments of bands	Dq cm <sup>-1</sup>	B cm <sup>-1</sup>	β	ν <sub>2</sub> /ν <sub>1</sub>	LFSE KJ mol <sup>-1</sup>
CoL(H <sub>2</sub> O)	(ν <sub>1</sub> )	8520	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)	968	798	0.84	92.66
	(ν <sub>2</sub> )	18110	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub>				
	(ν <sub>3</sub> )	19420	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)				
		31500	CT-band				
NiL(H <sub>2</sub> O)	(ν <sub>1</sub> )	10420	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)	1042	655	0.62	149.5
	(ν <sub>2</sub> )	17860	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)				
	(ν <sub>3</sub> )	23260	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)				
CuL(H <sub>2</sub> O)		14320	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	-	-	-	103.4
		26300	CT-band				

complexes show a number of bands in the region 500–200 cm<sup>-1</sup> and therefore it becomes difficult to assign bands to the metal-ligand vibrations.

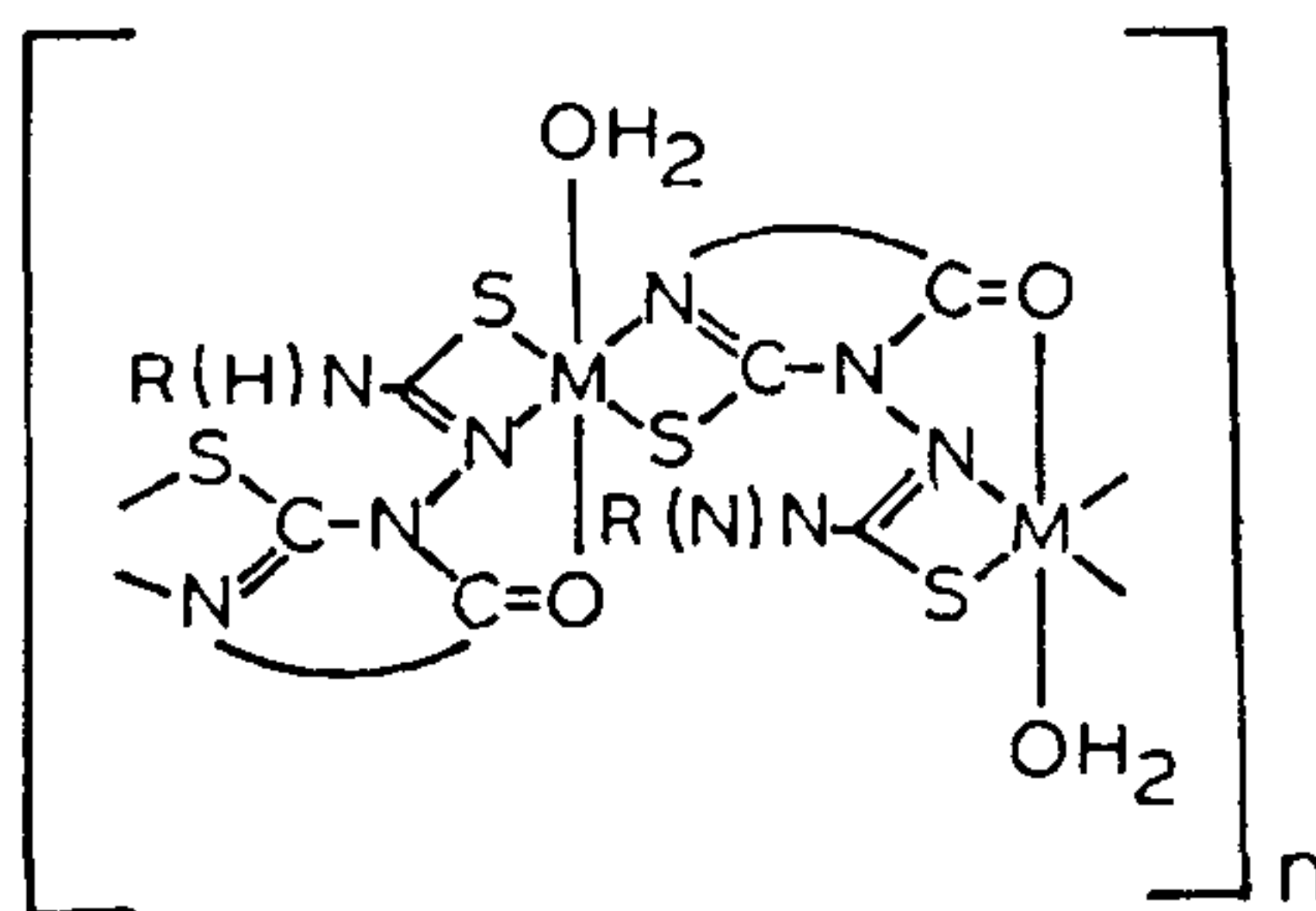
The <sup>1</sup>H NMR spectrum of the ligand shows multiplet at 4.16 and 4.60 assignable to two allylic (-CH<sub>2</sub>-CH=) and two vinylic (-CH=CH<sub>2</sub>) protons respectively. One vinylic (-CH=CH<sub>2</sub>) and four aromatic protons appear as multiplet at 5.68 and 7.80 respectively. The broad signal at 6.12 in the ligand could be due to the NH proton. This undergoes only a small downfield shift on complexation indicating that the NH group does not participate in coordination. The signal at 1.98 in the ligand, assignable to the SH protons, disappears in the complexes suggesting deprotonation of the mercaptan groups during formation of the complexes.

The interpretation of the magnetic and the electronic data is based on the earlier report<sup>6</sup>. The observed magnetic moment (4.93 B.M.) of the cobalt(II) complex suggests the formation of a high-spin octahedral complex with high orbital contribution attributable to the three-fold degeneracy of the <sup>4</sup>T<sub>1g</sub> ground term. The μ<sub>eff</sub> value (2.92 B.M.) observed for the nickel(II) complex indicates an octahedral geometry around the nickel(II) ion. The copper(II) complex shows a magnetic moment of 1.98 B.M. which is consistent with the presence of one unpaired electron. The excess over spin-only value is accounted for the presence of large Jahn-Teller effect. The ESR spectrum of the copper(II) complex shows a trend g<sub>11</sub>(2.198) > g<sub>1</sub>(2.008) > g<sub>z</sub>(2.0023) showing that the unpaired electron is localized in the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital and that the spectrum is characteristic of axial symmetry. Further, g<sub>11</sub> < 2.3 indicates a covalent environment in the complex around the copper(II)

ion. The zinc and cadmium complexes are diamagnetic.

The electronic spectral data (table 2) of cobalt(II) and nickel(II) complexes show an octahedral geometry. The band positions and assignments are presented in table 2. In the case of cobalt(II) complex the transition (ν<sub>2</sub>), <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>, could not be seen because of its very low intensity. However, the position was calculated and is reported in table 2. The spectrum of copper(II) complex suggests a distorted octahedral geometry. The absence of a band below 10,000 and above 17,000 cm<sup>-1</sup> rules out the possibility of a tetrahedral or square planar symmetry. The solution spectrum in DMF of the copper(II) complex also exhibits a single broad band at 13,500 cm<sup>-1</sup>. The computed ligand field parameters (table 2) support the proposed octahedral geometry.

On the basis of the analytical, solubility, magnetic and spectral data, a ligand bridged polymeric octahedral structure (figure 2) has been proposed to the



M = Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)  
R = -CH<sub>2</sub>-CH=CH<sub>2</sub>

Figure 2.

cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes with  $H_2L$  which behaves as a pentadentate biprotic ligand and the sixth coordination position is occupied by the water molecule.

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## BIFLAVONES FROM THE LEAVES OF *RHUS ALATA* THUMB.

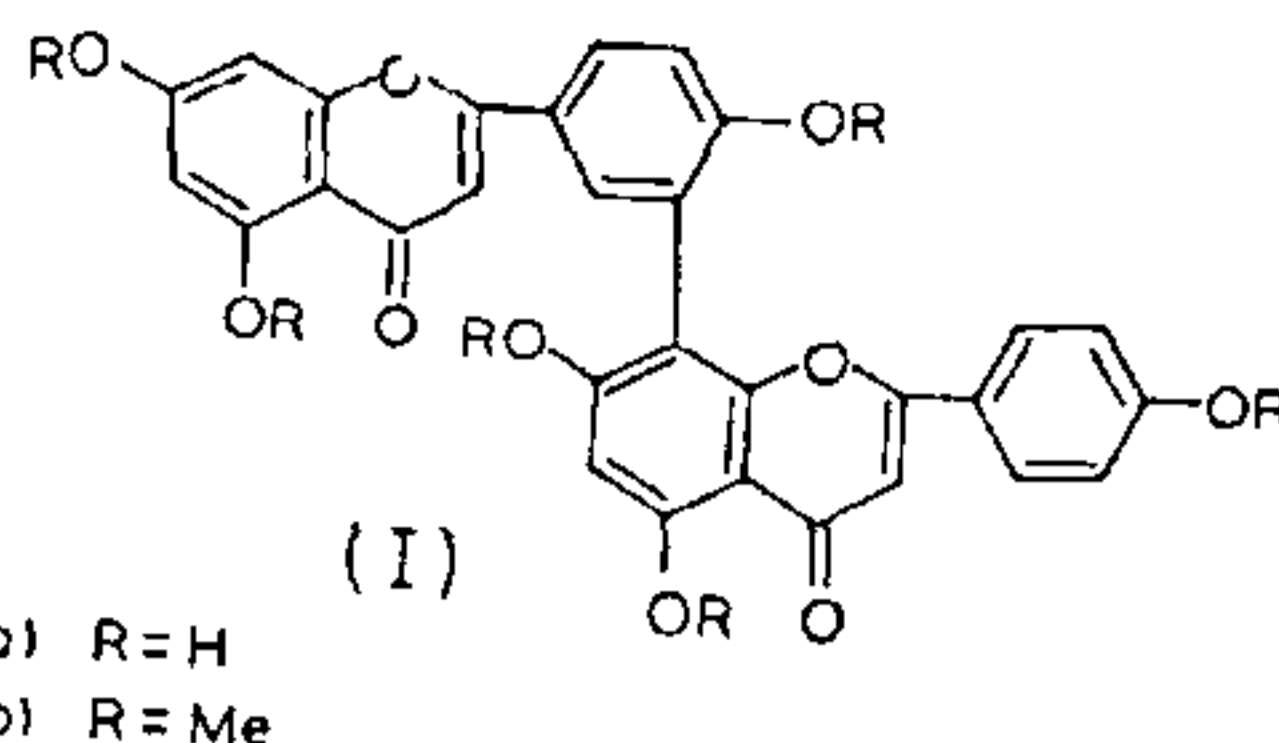
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The chemotaxonomic significance of biflavones in the genus *Rhus*, the cardiotoxic activity of the Chinese syrup "Shu Guang Tong" prepared from the extract of *R. Chinensis*<sup>1,2</sup> and the isolation of allergens from *R. toxicodendron*<sup>3</sup> prompted us to investigate *Rhus alata* (Syn. *Hippobromus alatus*) Thumb. which has not been reported so far. A number of biflavones have been reported from *R. succedanea*<sup>4-12</sup>, *R. toxicodendron*<sup>13</sup>, *R. punjabensis*<sup>14</sup> and *R. mysurensis*<sup>15</sup>. In the present communication, we report the occurrence of biflavones from the leaves of *R. alata*.

*R. alata* Thumb. was collected from the Pucchung University College, Aizaul, Mizoram and identified by Dr W. Husain, Department of Botany of this University. A voucher specimen was submitted to the University Herbarium, (Voucher Number, Husain-33701).

The dried and powdered leaf material of *R. alata* (1 kg), after being defatted with light petrol, was



extracted with EtOH. The EtOH extract was concentrated and the residue refluxed with light petrol and benzene; treated with boiling water and filtered. The yellow solid, undissolved residue (0.5 g) yielded the two chromatographically homogeneous fractions RA-I ( $R_f$  0.16) and RA-II ( $R_f$  0.34) after development on a silica gel column and subsequent preparative TLC [silica gel, benzene-pyridine-formic acid (BPF), 36:9:5].

RA-I; RA-I was comparable with amentoflavone on TLC (silica gel, BPF, 36:9:5). On methylation it gave a mixture of hexamethyl ethers of amentoflavone, agathisflavone and robustaflavone which were separated by preparative TLC (silica gel, BPF, 36:9:5). The minor constituents were tentatively characterized as hexamethyl ethers of agathisflavone and robustaflavone, based on their  $R_f$  values and characteristic shade in UV light with authentic sample<sup>16,17</sup>. Amentoflavone hexamethyl ether (Ib) was characterized by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ -scale); 3.80 (s, 6H, OMe-4, 4''), 3.86 (s, 3H, OMe-7), 3.94 (s, 3H, OMe-7''), 3.96 (s, 3H, OMe-5), 4.10 (s, 3H, OMe-5''), 6.40 (d, 1H, J=3Hz, H-6), 6.54 (d, 1H, J=3Hz, H-8), 6.54 (s, 1H, H-6''), 6.56 (s, 2H, H-3, 3''), 7.18 (d, 1H, J=9Hz, H-3''', 5'''), 7.18 (d, 1H, J=9Hz, H-5'), 7.44 (d, 2H, J=9Hz, H-2''', 6'''), 7.90 (d, 1H, J=3Hz, H-2') and 8.04 (dd, 1H, J=9Hz & 3Hz, H-6'). Therefore, the major constituent in RA-I was characterized as amentoflavone (Ia)<sup>18</sup>.

RA-II; RA-II was comparable with hinokiflavone on TLC (silica gel, BPF, 36:9:5). On methylation by the method of Khan *et al*<sup>16</sup> it gave hinokiflavone pentamethyl ether. On acetylation using acetic

