

alanine, which occurred in moderate amounts in the whole body extract of the larvae and varied marginally during metamorphosis, were present in high concentrations in the hydrolysate of web (ca. 80%). Presence of high amounts of glycine, alanine and serine in the silk proteins of several insects has been reported³. On the other hand, glutamic acid and proline, the principal components of body pool amino acids, together contributed merely 6% to the total content of web amino acids. Thus, the most abundant amino acids of the whole body extract, that underwent dramatic changes at the time of metamorphosis, were not utilised extensively for the synthesis of web proteins.

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PAPER CHROMATOGRAPHY OF METAL ION COMPLEXES WITH MORPHOLINE-4- CARBODITHIOATE

THE bidentate chelating system $\text{>N}-\text{C} \begin{matrix} \text{S} \\ \text{S}^- \end{matrix}$ present in morpholine-4-carbodithioate was used for complexation with Fe(III), Co(III), Ni(II), Cu(II), Ru(III), Rh(III), Pd(II), Ir(III), Pt(IV) and Te(IV). The paper chromatographic detection and separation of above metal ions on paper strips was

found quite successful. The coloured spots of the complexes were clearly visible without use of any spraying agent. Maximum three or four complexes could be identified and separated on paper strip.

The reaction of the ligand with metal ions is not selective, therefore the separation of complexes using masking agents and pH control requires more labour, steps and time. The chromatographic behaviour of morpholine-4-carbodithioate metal complexes have not been studied previously. Some references are available for the metal chelates¹⁻⁶ with this reagent. Present communication describes the paper chromatographic separation and identification of the complexes of Fe(III), Co(III), Ni(II), Cu(II), Ru(III), Rh(III), Pd(II), Ir(III), Pt(IV) and Te(IV) with morpholine-4-carbodithioate.

Experimental

Potassium salt of the reagent was prepared by mixing potassium hydroxide, morpholine and carbon-disulphide in 1 : 1 : 1 ratio in ether at 0° C, 1% (w/v) solution (KMCDT) was prepared in distilled water.

The complexes were isolated in aqueous medium by mixing solutions in stoichiometric ratios (ligand in slight excess). The chelates were filtered, washed with ether and dried at 110–120° C. In the case of Co(mcdt)₃ rapid oxidation of Co(II) into Co(III) takes place.

The complexes were analysed for carbon, hydrogen and nitrogen contents and their composition corresponded to M (C₅H₈ONS₂)_n. Spectral studies were also made in the range 200 cm⁻¹–4000 cm⁻¹. Conductivity measurements of the complex solutions in nitrobenzene were made on Toshniwal CLOI/OIA conductivity bridge using dip type cell (K = 0.74) (Table I).

For the purpose of putting spots, most of the complexes were dissolved in chloroform at room temperature. Owing to the insolubility of Pd(II) and Ni(II) the complexes were prepared on paper strips. The chromatographic chamber was saturated with the vapours of the developer for at least one day. Chromatography was carried out on Whatman No. 1 filter paper strips (3 cm × 15 cm) using the ascending technique. The sample solution was applied at a point 2 cm from the end, and the developer was allowed to travel for about 10 cm from the point of application of the spot. The time required for the different metal complexes was noted. The R_f values of the complexes in different solvents are recorded in Table II.

TABLE I
Elemental analysis and spectral studies

Compound	Elemental analysis Found (Calc.)			I.R. spectra (cm ⁻¹)			λ M (mhos)
	C%	H%	N%	C...N	C...S	M...S	
Kmdtc	27.10 (27.14)	4.39 (4.59)	6.15 (6.38)	1440	990
Fe (mcdt) ₃	32.5 (32.2)	4.30 (4.40)	7.62 (7.70)	1480	1000	330	0.74
Co (mcdt) ₃	32.80 (33.00)	4.68 (4.40)	7.52 (7.70)	1470	1005	358	0.89
Ni (mcdt) ₂	31.30 (31.30)	4.48 (4.18)	7.18 (7.30)	1450	1010	386, 374	0.66
Cu (mcdt) ₂	30.28 (30.90)	4.45 (4.13)	7.10 (7.20)	1440	1010	342	1.04
Ru (mcdt) ₃	29.95 (30.64)	4.15 (4.11)	6.92 (7.14)	1500	1020	340, 320	2.22
Rh (mcdt)	30.40 (30.55)	4.32 (4.10)	7.20 (7.12)	1480	1010	355	0.89
Pd (mcdt) ₂	27.60 (27.87)	3.90 (3.74)	6.43 (6.50)	1495	1010	345	0.15
Ir (mcdt) ₃	26.35 (26.53)	3.76 (3.56)	6.06 (6.18)	1495	1000	320	0.30
Pt (mcdt) ₃ Cl	24.55 (25.10)	3.38 (3.48)	5.71 (5.85)	1500	1005	340	0.15
Te (mcdt) ₄	30.95 (30.93)	4.15 (4.15)	7.07 (7.20)	1480	1000	..	0.44

TABLE II
Spot colour, λ_{max} and R_f values of the metal ion complexes

Complex	Spot colour	λ _{max}	MeOH	n-PrOH	Aq. n-BuOH	Aq.	Aq.	Aq.
						n-BuOH + AcOH (4:1) (v/v)	n-BuOH + CHCl ₃ (7:3) (v/v)	n-BuOH + CHCl ₃ (4:1) (v/v)
Fe (mcdt) ₃	Grey	520	0.55	0.92	0.97	0.93	0.97	0.98
Co (mcdt) ₃	Green	500	0.44	0.80	0.90	0.61	0.88	0.99
Ni (mcdt) ₂	Yellowish green	480	0.00	..	0.00	0.00	0.00	..
Cu (mcdt) ₂	Brown	460	0.67	0.65	0.99	0.59	0.75	0.65
Ru (mcdt) ₃	Black	470	0.00	0.00	..	0.80	0.98	0.99
Rh (mcdt) ₃	Orange	510	0.33	0.00	0.76	0.90	0.45	0.85
Pd (mcdt) ₂	Yellow	490	0.00	..	0.00	0.00	0.00	0.00
Ir (mcdt) ₃	Yellowish orange	430	0.32	0.00	0.74	0.80	0.95	0.92
Pt (mcdt) ₃ Cl	Yellow	440	0.65	..	0.00	0.00	0.00	0.00
Te (mcdt) ₄	Yellow	450	0.85	0.99	0.94
Developing Time (Minutes)			15	30	45	45	45	45
Room Temperature = 32° C.								

Result and Discussion

R_f values of the chelates (Table II) in methanol, *n*-propanol, aq. *n*-butanol, aq. *n*-butanol + acetic acid (4 : 1 v/v), aq. *n*-butanol + chloroform (7 : 3 v/v) and aq. *n*-butanol + chloroform (4 : 1 v/v) show that the various ternary and quaternary mixtures of the complexes can be quite successfully resolved. The maximum trailing effect was observed in acetic acid and chloroform, it was reduced when mixed with *n*-butanol. The R_f values in mixtures are close to those obtained with the single compound. The high R_f values in dioxane, acetone and chloroform may be due to the solubility effect. During the process, it has also been observed that the colour of the spots in different solvents remain unchanged.

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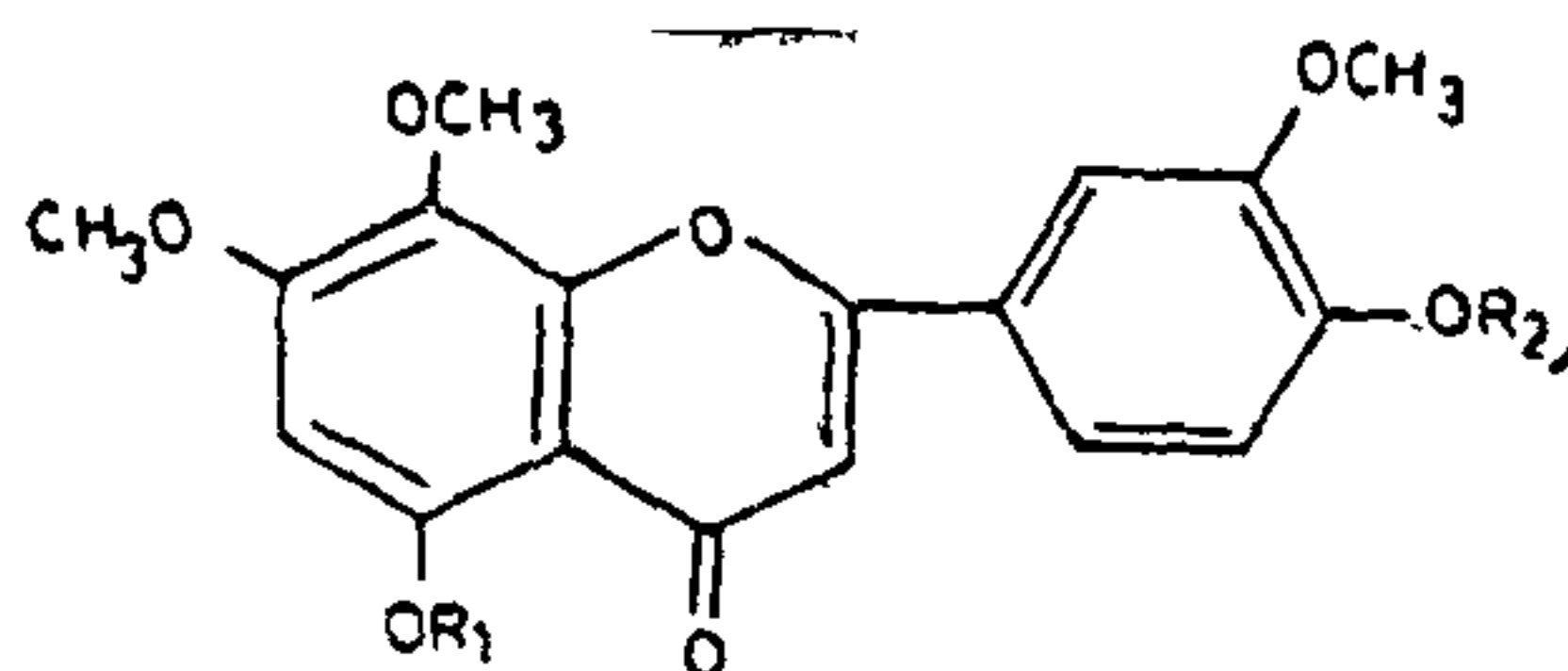
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FLAVONE FROM *LYCHNOPHORA AFFINIS*: A SYNTHETIC STUDY

CONSTITUTION of *Lychnophora affinis* flavone as 5, 4'-dihydroxy-7, 8, 3'-trimethoxyflavone (I) needs revision as its properties are different from the sample obtained synthetically.

Based on a study of the colour reactions and spectral data, a new flavone isolated from *Lychnophora affinis* was assigned its constitution as 5, 4'-dihydroxy-7, 8, 3'-trimethoxyflavone¹ (I). This communication reports the synthesis of this flavone using 2'-hydroxy-3, 3', 4', 6'-tetramethoxy-4-benzyloxychalkone which itself was obtained from 2-hydroxy-3, 4, 6-trimethoxyacetophenone² and *O*-benzylvanillin³. Selenium dioxide oxidation of the chalkone yielded 5, 7, 8, 3'-tetramethoxy-4'-benzyloxyflavone (II). Catalytic debenylation of II followed by the subsequent selective demethylation of the resulting 5, 7, 8, 3'-tetramethoxy-4'-hydroxyflavone (III) gave the required 5, 4'-dihydroxy-7, 8, 3'-trimethoxyflavone (I) which on acetylation yielded its diacetate (IV). Since the properties

observed for the synthetic dihydroxytrimethoxyflavone (I) [m.p. 235-37°; UV (MeOH): 275, 295 (sh.), 360 nm; + AlCl₃: 285, 305 (sh), 409 nm; + AlCl₃ + HCl: 283, 307 (sh), 405 nm] are different from those reported¹ for the natural sample [m.p. 163-66°; UV (MeOH): 255, 270 (sh), 355 nm; + AlCl₃: 270, 357, 400 nm; + AlCl₃ + HCl: 263, 275 (sh), 357, 400 nm], the constitution assigned to the¹ *L. affinis* flavone needs revision.



- I. $R_1 = R_2 = H$
- II. $R_1 = CH_3$; $R_2 = CH_2Ph$
- III. $R_1 = CH_3$; $R_2 = H$
- IV. $R_1 = R_2 = COCH_3$

Experimental

2'-Hydroxy-3, 3', 4', 6'-tetramethoxy-4-benzyloxychalkone

A solution of 2-hydroxy-3, 4, 6-trimethoxyacetophenone² (1 g) in ethanol (15 ml) and *O*-benzylvanillin³ (1.3 g) was treated with aqueous-ethanolic solution of potassium hydroxide (2 g), left at room temperature for 48 hrs and then acidified with hydrochloric acid. The chalkone thus obtained was filtered out, washed and dried. It crystallised from ethanol as yellow needles (1.1 g), m.p. 153-54°, analysed for C₂₆H₂₆O₇ and gave positive ferric reaction.

5, 7, 8, 3'-Tetramethoxy-4'-benzyloxyflavone (II)

A mixture of the above chalkone (1.0 g), selenium dioxide (1.7 g) and isozmyl alcohol (40 ml) was refluxed for 24 hrs and then filtered to remove selenium metal and its dioxide. Removal of the solvent from the filtrate gave the flavone (II) that crystallised from benzene-acetone as colourless needles (0.8 g), m.p. 198-99°, analysed for C₂₈H₂₈O₇, and gave negative ferric reaction. I.R. (KBr) 1639, 1600, 1515, 1460, 1418, 1379, 1342, 1266, 1242, 1212, 1170, 1149, 1130, 1111, 1047, 1026, 1000, 977, 957, 922, 873, 847, 813 cm⁻¹. N.M.R. (δ , CDCl₃, TMS as internal standard) 3.98 (12 H, s, 4X—OCH₃), 5.23 (2H, s, —CH₂C₆H₅), 6.41 (1H, s, C₃—H), 6.62 (1H, s, C₆—H), 7.09 (1H, d, J = 9Hz, C₅'—H), 7.46-7.64 (7H, m, C₂'—H, C₄'—H and —CH₂C₆H₅).