

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.

Department of Chemistry,
Hindu College,
Moradabad 244 001,
December 22, 1977.

RAVINDRA KUMAR.
NEPAL SINGH.

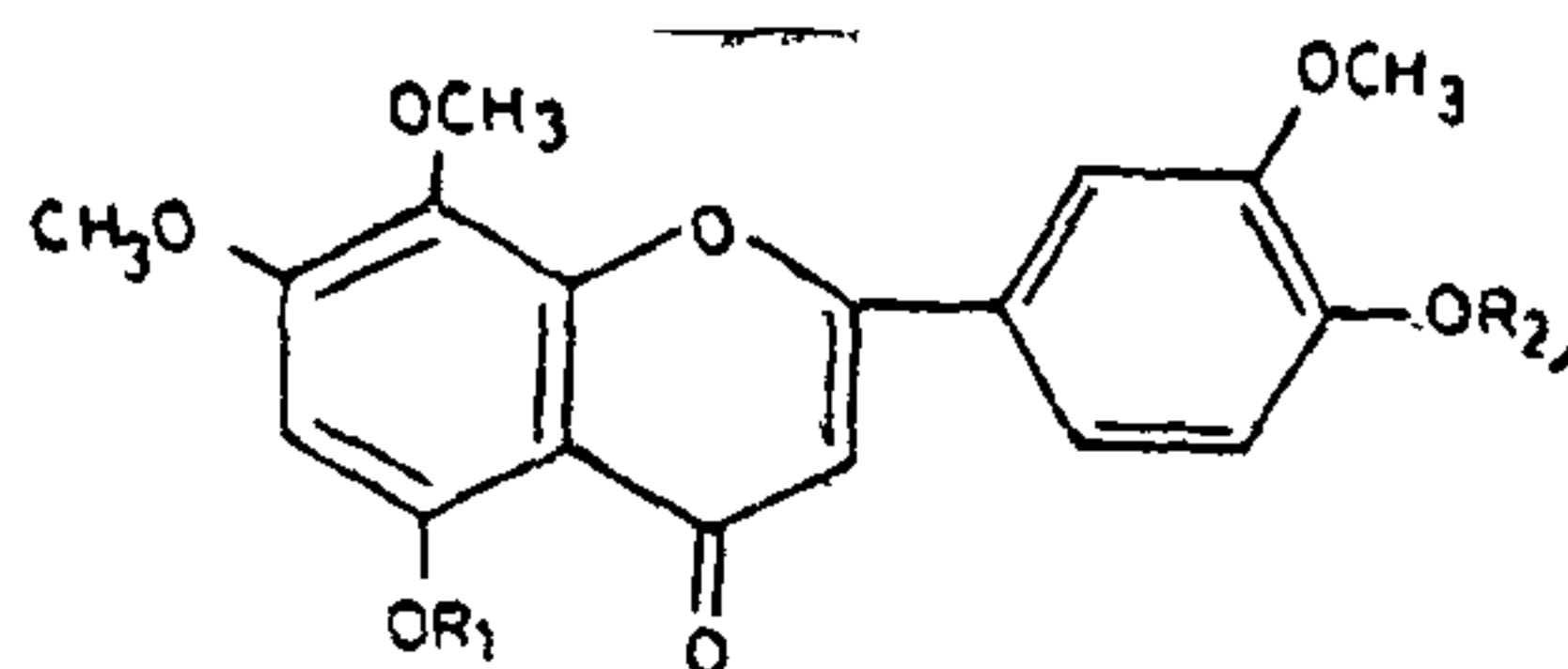
1. Aravamudan, G., Brown, D. H. and Venkappayya, P., *J. Chem. Soc. (A)*, 1971, 2744.
2. Hulanick, A. *Talanta*, 1967, 14, 1371.
3. Nikolov, G. St., Jordanov, N. and Havezov, I. J., *Inorg. Nucl. Chem.*, 1971, 33, 105.
4. Critchlow, P. B. and Robinson, S. D., *J. Chem. Soc. (A)*, 1975, 1367.
5. Sceney, C. G. and Maghee, R. J., *Inorg. Nucl. Chem. letters*, 1973, 9, 595.
6. Singh, N., Kumar, R. and Agarwal, R. C., *Curr. Sci.*, Dec. 1977, 46.

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).

5, 7, 8, 3'-Tetramethoxy-4'-hydroxyflavone (III)

A solution of the benzyloxytetramethoxyflavone (II) (0.7 g) in ethyl acetate (80 ml) was treated with Pd-C (0.4 g) and then stirred in an atmosphere of hydrogen till absorption completed. The catalyst was filtered out. Removal of the solvent from the filtrate gave hydroxytetramethoxyflavone (III) which crystallised from benzene as colourless needles (0.3 g), m.p. 222° and analysed for C₁₉H₁₈O₇.

5, 4'-Dihydroxy-7, 8, 3'-trimethoxyflavone (I)

A solution of the monohydroxytetramethoxyflavone (II) (0.2 g) in acetonitrile (15 ml) was treated with anhydrous aluminium chloride (0.2 g) and then refluxed for 4 hr., and the solvent was distilled off under reduced pressure. On acidification with hydrochloric acid, the demethylation product was obtained as yellow solid which was filtered, washed and dried. It crystallised from ethyl acetate to give 5, 4'-dihydroxy 6, 7, 3'-trimethoxyflavone (I) as light yellow needles, m.p. 235-37°, analysed for C₁₈H₁₆O₇ and gave positive ferric reaction. The melting point and UV spectral data observed for the synthetic sample was significantly different from those reported¹ for the natural sample. I.R. (KBr) 3185, 1667, 1600, 1550, 1506, 1429, 1370, 1333, 1304, 1263, 1227, 1208, 1183, 1130, 1020, 962, 858, 808 cm⁻¹.

5, 4'-Diacetoxy-7, 8, 3'-trimethoxyflavone (IV)

The dihydroxytrimethoxyflavone (I) (0.04 g) was treated with acetic anhydride (1.00 ml) and pyridine (0.50 ml), warmed in a water bath to obtain a clear solution and then left overnight. It was treated with ice and the acetate (IV) thus obtained was filtered, washed and dried. The acetate (IV) crystallised from ethyl acetate-petroleum ether as colourless microprisms, m.p. 180-81°. It analysed for C₂₂H₂₀O₉. NMR (δ, CDCl₃, TMS as internal standard): 2.33 (3H, s, C₆-OCOCH₃), 2.42 (3H, s, C₈-OCOCH₃), 3.96 (9H, s, 3X - OCH₃), 6.56 (1H, s, C₅-H), 6.60 (1H, s, C₆-H), 7.23 (1H, d, J = 9Hz, C_{5'}-H), 7.46 (2H, m, C₇-H and C₈-H).

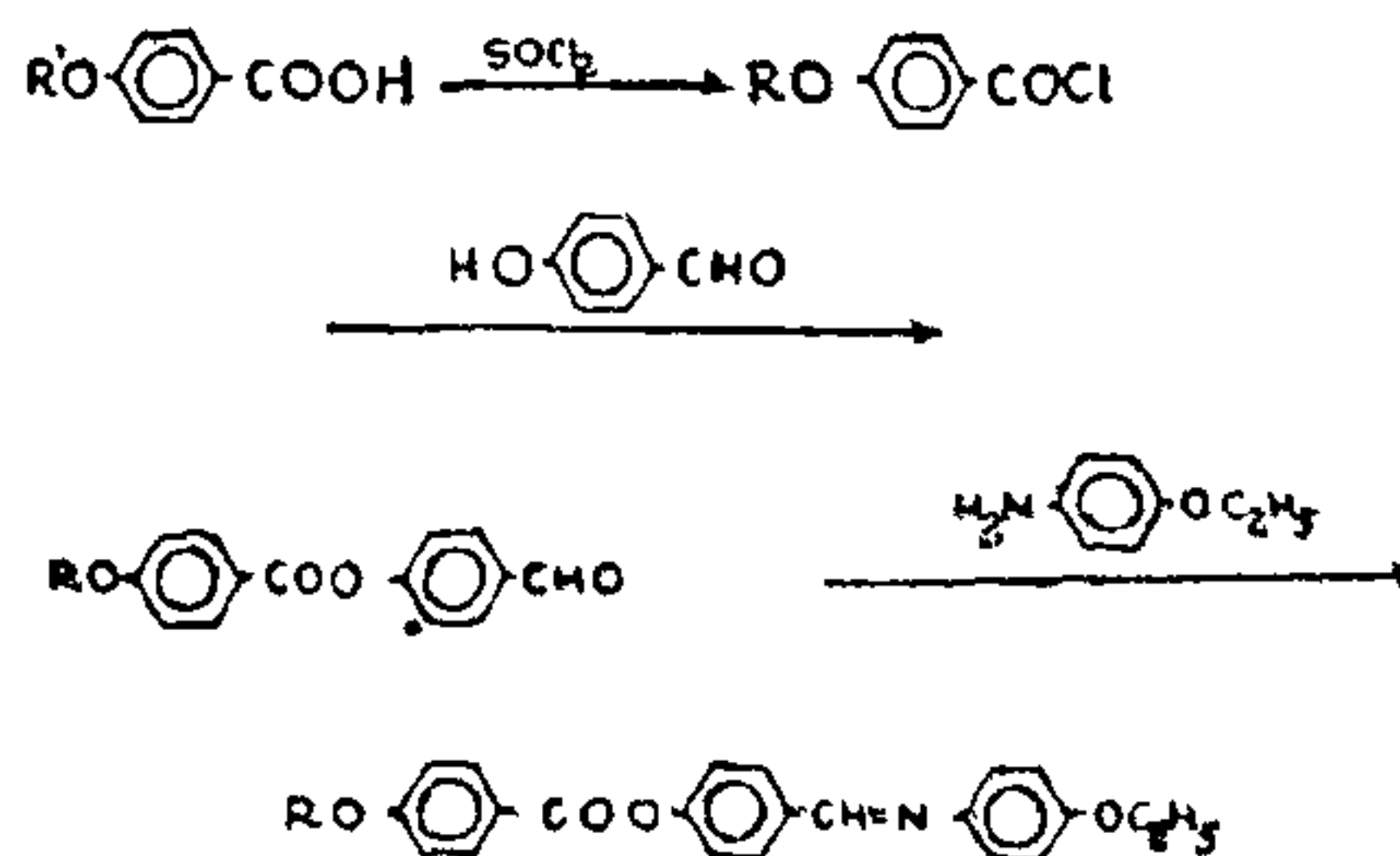
Department of Chemistry,
University of Delhi,
Delhi 110 007,
December 8, 1977.

D. K. BHARDWAJ,
A. K. GUPTA,
R. K. JAIN,
G. C. SHARMA.

1. LeQuesene, P. W., Pastore, M. P. and Raffauf, R. F., *Lloydia*, 1976, 39, 391.
2. Baker, W., *J. Chem. Soc.*, 1941, p. 605.
3. Lovacy, A., Robinsin, R. and Sugawara, S., *Ibid.*, 1930, p. 817.

MESOMORPHIC BEHAVIOUR OF SOME SCHIFF
BASE ESTERS: *p*(*p'*-*n*-ALKOXYBENZOYLOXY)
BENZYLIDENE-*p''*-PHENETIDINES

A NUMBER of mesomorphic substances are synthesized having different functional groups and molecular geometry. Most of these are Schiff bases, acids, and esters. Comparatively a few mesomorphic homologous series comprising both an ester linkage (-COO-) and an azomethine (-CH=CH-) group in the same molecule have been studied. Dave and Patel¹ and Fishel and Patel² studied the homologous series of Schiff base aliphatic esters. Gray and Harrison³ studied different *p*-substituted benzylideneamino-cinnamates of alkyl and aryl esters. These exhibit smectic and nematic mesophases. Dave and Kurian⁴ have recently studied the mesomorphic homologous series *p*(*p'*-*n*-alkoxybenzoyloxy) benzylidene-*p''*-anisidines and *p*(*p'*-*n*-alkoxybenzoyloxy) benzylidene-*p''*-toluidines. These exhibit smectic and nematic mesophases with good phase length. A change in molecular structure may bring about an appreciable change in the general mesomorphic behaviour. To further investigate the effect of change in molecular structure we have studied the mesomorphic behaviour of some compounds of the series, *p*(*p'*-*n*-alkoxybenzoyloxy) benzylidene-*p''*-phenetidines. These compounds are prepared by the following synthetic route.



The mesomorphic properties of these compounds have been investigated with a Leitz Ortholux Polarizing Microscope equipped with Leitz heating stage. The melting points and the transition temperatures of these compounds are compiled in the table. The

TABLE
p(*p'*-*n*-alkoxybenzoyloxy) benzylidene-*p''*-phenetidines

Compound No.	Alkyl group R	Transition temperature (°C)		
		Smectic	Nematic	Isotropic
1	C ₁₀ H ₂₁	110.5	113.5	233.0
2	C ₁₁ H ₂₃	104.5	133.0	219.0
3	C ₁₁ H ₂₃	102.5	148.0	210.5
4	C ₁₄ H ₂₉	103.0	157.0	203.0
5	C ₁₆ H ₃₇	102.0	160.0	192.5