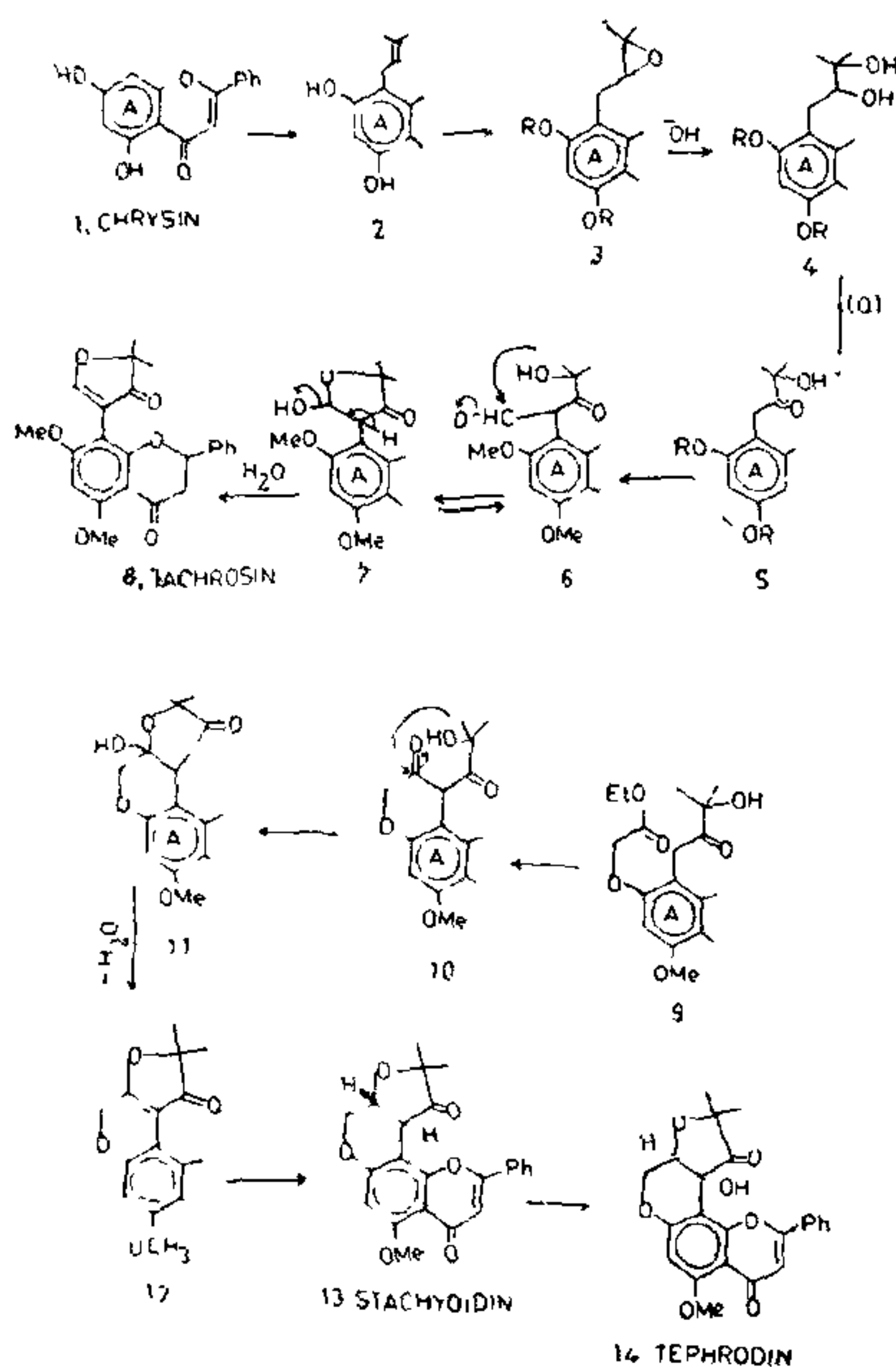


### A POSSIBLE BIOGENESIS OF THE NOVEL TYPE OF FLAVONES FROM *TEPHROSIA* *POLYSTACHYOIDES*

FROM *Tephrosia polystachyoides*, three flavones have recently been isolated by African workers<sup>1,2</sup> called tachrosin, stachyoidin and tephrodin which have been given structures as 8, 13 and 14 respectively. They represent novel types of flavonoids, the former containing one additional C-6 unit in the form of 2, 3-dihydro-2, 2-dimethyl-3-oxo-4-furyl unit and the latter an additional C-7 unit in the form of furo-pyran ring system. We suggest here that all the three compounds could be explained to be evolved biogenetically from naturally occurring chrysin (1) as illustrated in the chart.



A BIOGENETIC SCHEME FOR THE EVOLUTION OF FLAVONES  
OF *T. POLYSTACHYOIDES*

C-Prenylation of chrysin in the 8-position gives 2; this is an established biological step in different flavonoids and was accomplished in the laboratory by Jain *et al.*<sup>3</sup> 2 undergoes oxidation to the corresponding glycol (4) via epoxide 3 which can subsequently undergo oxidation to give 8-(3-hydroxy-3-methyl-2-oxobutyl) derivative (5). The dimethyl ether of 5 can undergo formylation of the side chain with formic acid or its biological equivalent at the benzylic

carbon to afford 6 which can cyclize to give 7. Final dehydration will yield tachrosin (8).

On the other hand, if the compound (5) is protected by ethoxycarbonylmethylation in the 7-position and by methylation in the 5-position (structure 9), intramolecular Claisen condensation can give rise to 3-pyranone derivative (10) which can cyclize to give 11. Subsequent successive steps of dehydration and *cis* reduction can give stachyoidin (13).

Final hydroxylation at the benzylic position of stachyoidin (13) can yield tephrodin (14) itself.

Synthetic studies based on the above biogenetic scheme are in progress.

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### OSCILLATORY REACTION—APPARENT ENERGY OF ACTIVATION

OSCILLATORY chemical reactions have reached the status of a branch of laboratory chemistry and therefore suggestions leading to further probes into the mechanism are always looked for. Exhaustive accounts of the different aspects of the oscillatory reactions are available<sup>1-3</sup>. Certain important features in the  $\text{IO}_3^- - \text{H}_2\text{O}_2$  system and  $\text{BrO}_3^- - \text{Mn(II)/Ce(III)}$  system have been reported by us<sup>4,5</sup>. The temperature coefficient and the apparent energy of activation for the overall process in oscillatory reactions have been evaluated<sup>6,7</sup>. The present letter deals with the determination of the apparent energy of activation of the overall process in the  $\text{BrO}_3^- - \text{malic acid}$  system involving Mn(II) or Ce(III) ions.

The oscillations in the concentration ratio of  $\text{Mn}^{3+}/\text{Mn}^{2+}$  or  $\text{Ce}^{4+}/\text{Ce}^{3+}$  are recorded using a  $x-t$  recorder. All the constituents except potassium bromate were kept thermostatted and stirred in a polythene beaker. The cell was constituted between a platinum indicator electrode and a saturated calomel electrode connected through a potassium nitrate salt bridge. The oscillations were triggered off with the addition of the last constituent namely potassium bromate previously thermostatted. The experiment was repeated at each temperature to ensure that the results were quite

TABLE I  
Composition of the reaction mixture

Constituent	Concentration (M)
KBrO <sub>3</sub>	0.05
H <sub>2</sub> SO <sub>4</sub>	2.23
Malic acid	0.05
Mn(II)/Ce(III)	0.003

TABLE II  
BrO<sub>3</sub><sup>-</sup> - Malic acid - Mn<sup>2+</sup> system—values of apparent energy of activation

Tempe- rature (°K)	Induc- tion time <i>t</i> secs.	Total dura- tion <i>t</i> secs.	Oscil- lating time <i>t</i> secs.	Time for 1-10 oscilla- tions <i>t</i> secs.	Time for 5th oscilla- tion <i>t</i> secs.
303	112	1464	1352	244	24
308	108	1370	1262	144	22
373	74	816	742	134	12
318	60	672	612	92	10
323	56	470	414	88	8
328	40	346	306	52	6
333	38	251	213	44	6
338	38	168	130	30	4
<i>E<sub>a</sub></i> (kcal/ mole)	8.7	12.0	11.9	11.7	10.5

TABLE III  
BrO<sub>3</sub><sup>-</sup> - Malic acid - Ce<sup>3+</sup> system—values of apparent energy of activation

Tempera- ture (°K)	Induc- tion time <i>t</i> secs.	Total dura- tion <i>t</i> secs.	Oscilla- ting time <i>t</i> secs.	time for 1-10 oscilla- tions <i>t</i> secs.	time for 1-5 oscilla- tions <i>t</i> secs.
298	240	1640	1400	1108	590
303	168	1000	882	678	386
308	108	668	560	410	216
313	62	398	336	252	122
318	50	258	208	160	84
323	34	170	136	136	56
328	26	124	98	98	40
333	16	66	50	60	24
<i>E<sub>a</sub></i> (kcal/ mole)	15.6	17.4	16.5	16.5	17.4

reproducible. The use of a polythene beaker and pre-treatment of the electrode were proved<sup>4,5</sup> to be essential to get reproducible results. The temperature was varied between 25 and 65° C. The composition of the solution employed is given in Table I.

The results obtained with the system BrO<sub>3</sub><sup>-</sup> - malic acid and Mn(II) or Ce(III) ion are presented in Tables II and III.

The apparent energy of activation for the overall process was calculated from the slope of the linear plot of log (1/*t*) against 1/*T*, on the basis that the rate constant is inversely proportional to the time (*t*). For this purpose the total duration, oscillating time, time for a definite number of oscillations, time for any particular oscillation during the initial stages and the induction time were considered. The value of *E<sub>a</sub>* for the manganous system is 11.2 ± 0.7 kcal/mole. For the system involving cerous ions the value turns out to be 16.5 ± 0.9 kcal/mole. The apparent energy of activation for the cerous system is higher than that for the manganous system by about 5 to 6 kcal/mole in all instances considering the different times (*t*).

Field<sup>8</sup> has suggested a qualitative mechanism to explain the oscillations and induction period in the BrO<sub>3</sub><sup>-</sup> - Ce(III) - malonic acid system. In the malic acid system the reactions are different. It is observed that the presence of Br<sub>2</sub> affects the oxidation of malic acid by Ce(IV) as well as Ce(III) by BrO<sub>3</sub><sup>-</sup>. So Br<sup>-</sup> will also have the same effect as it is immediately converted to Br<sub>2</sub>.

We have found that the presence of Br<sup>-</sup> or Br<sub>2</sub> accelerates the oxidation of malic acid by Ce(IV). When the oscillatory reaction is started there is only a small amount of Br<sub>2</sub> present and so the oxidation of malic acid is slow and causes an induction period. Once an oscillation is over, sufficient amount of Br<sub>2</sub> is built up, the reaction proceeds faster and hence the induction does not appear for the subsequent oxidation of malic acid being slow compared to the oxidation of Ce(III). This is further confirmed by the decrease in the induction period in presence of Br<sup>-</sup> or Br<sub>2</sub> initially added to the system. Thus the oxidation of the organic acid by Ce<sup>4+</sup> is the controlling step, the temperature coefficient of which is reflected in the induction time and oscillation time.

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**PALEOECOLOGICAL-ECOLOGICAL  
INTERPRETATION OF SEDIMENTS OF  
MANGALORE HARBOUR AREA, WEST  
COAST OF INDIA ON THE BASIS OF  
COLOUR VARIATION OF OSTRACODA  
SHELLS**

*Introduction*

OVER 500 sedimentary samples drawn from 30 bore holes ranging in depth from 20 to 120 ft., in the area (Fig. 1) have yielded nearly 2500 ostracoda shells belonging to 53 species. These shells show colour variation—colourless, milky white, yellow, yellowish brown and black. Colour variation is noticed even

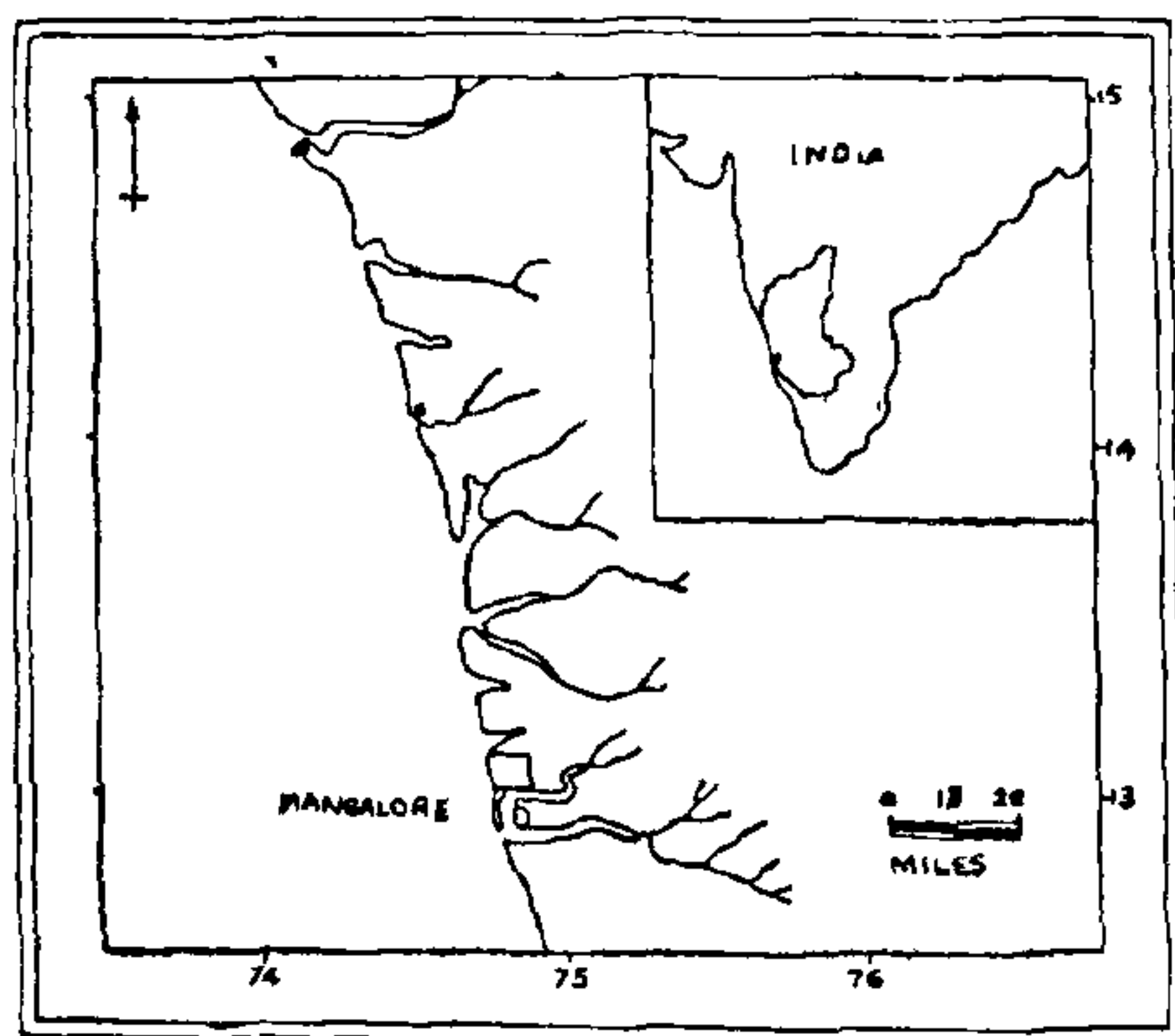


FIG. 1. Location Map.

in larva and juvenile forms. Detailed investigation has shown that 60% of the shells show colour variation and the remaining 40% are colourless. Shells showing different colours have been subjected to chemical test and it is found that different colours

are not of surface coating but genuine (Riley<sup>3</sup>). Examination of specimens under the Stereo-binocular microscope, both in reflected and transmitted light indicates that under the reflected light shells showing different colours appear transparent while the black or pyritised shells remain dull or opaque. However, under the liquid media in transmitted condition, pyritised shells behave transparent to translucent (Table I).

TABLE I

Total No. of Shells	Colourless	White to milky white	Yellowish to brown	Black or pyritised
2500	900	750	580	270
100%	36%	30%	24%	10%

*Discussion*

Colour diversity in ostracoda shells has been recently utilised to interpret paleoecology-ecology of the sediments and environment of deposition. The factor of colour variation in these shells has further revealed that the majority of the coloured shells which exhibit whitish to milky-white, yellowish-brown to brown, occur in sandy to sandy clayey sediments enriched with heavy minerals such as hematite, limonite, magnetite, zircon, garnet, micas and tourmaline. This indicates that the background colour is an environmental stimulus and the fauna might have responded to the colour of the surroundings by changing their own colour. This also suggests that the fauna has absorbed the dissolved Fe-Mg material in the form of food and hence, their colouring of the shells (Blackwealder<sup>1</sup>). White to light brown colour of the shells must have been formed in normal oxygenated environment, where the sediments are rich in Fe-material. On the other hand, pyritised shells are confined to the clayey sediments containing small granules of pyrite and carbonaceous matter. Colour variation in this case is attributed to the influence of sulphide material (Oerth<sup>2</sup>). Dominance of white, yellowish and brown coloured shells in the region is typical of fluctuating marine deltic environmental condition (Vanstraten<sup>4</sup>).

*Conclusion*

The sediments under investigation contain good preservation of ostracoda shells. In the assemblage 60% of the shells show colour variation milky white, yellowish, brownish yellow, brown, and the remaining, 40% of the shells are colourless. Data on colour ratio suggest that the deposition of the sediments has taken place in a shallow marine to fluctuating-estuarines