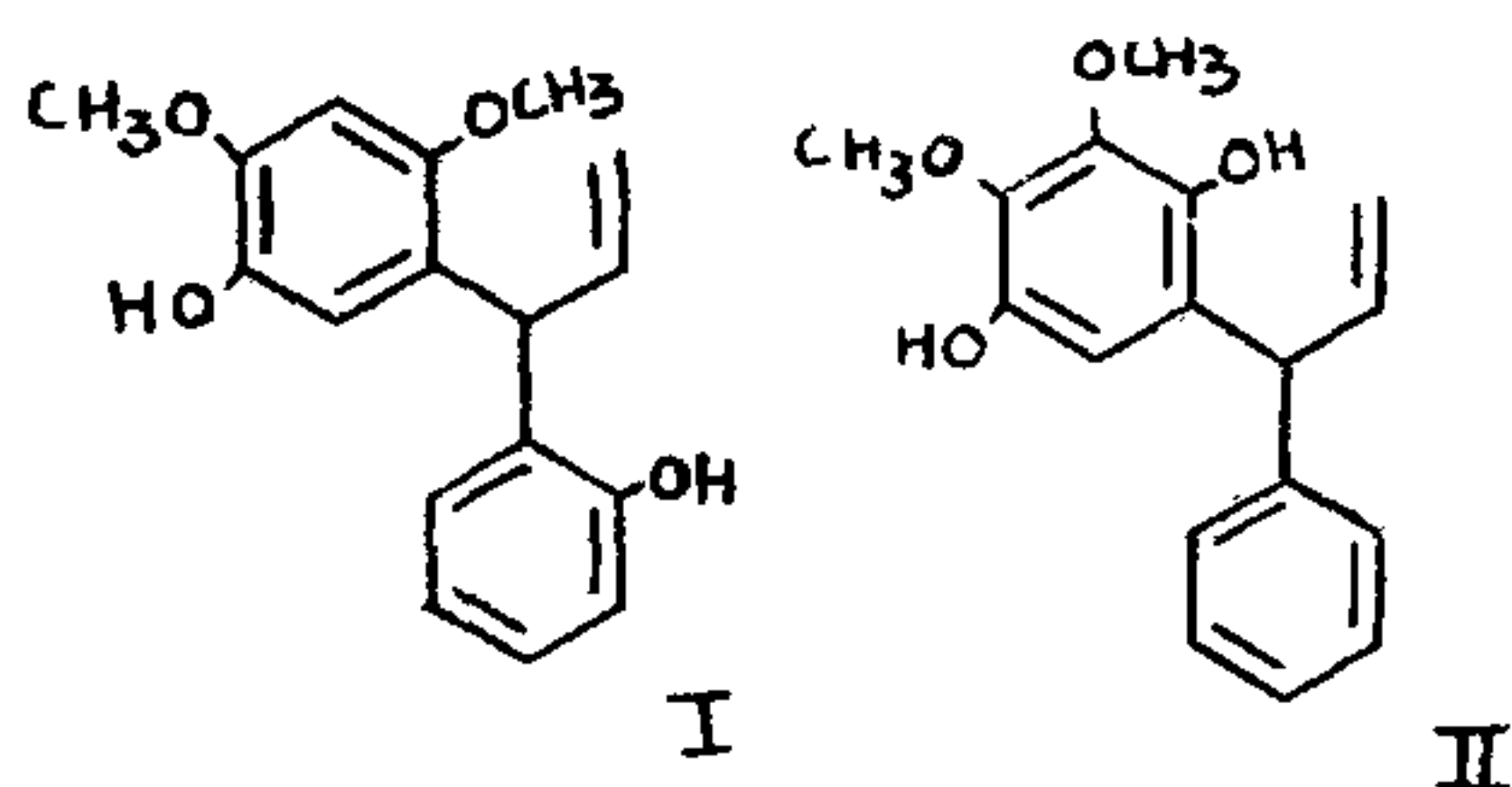


4-PHENYL COUMARINS AS PRECURSORS OF NEOFLAVANOIDS

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THE neoflavanoids¹ are a recent group of naturally occurring C₁₅-phenolic compounds comprising of 4-phenyl coumarins, 3, 3-diphenyl allyl compounds and allyl quinones (dalbergenones). Although a number of 4-phenyl coumarins and dalbergenones are known, so far only two examples of allyl phenols have been found in nature. These are (a) latifolin (I) and (b) the quinol (II).



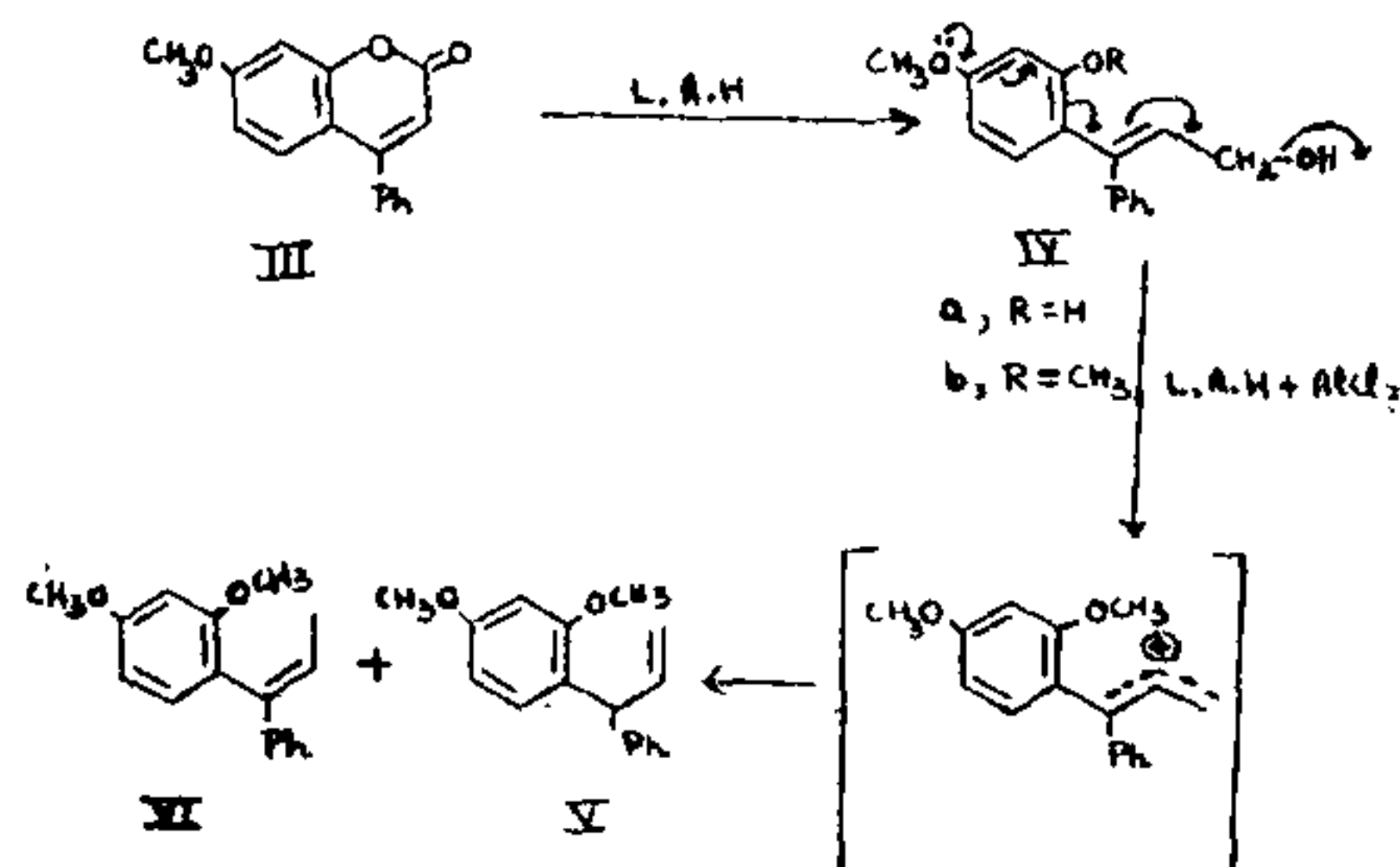
Eyton *et al.*² consider these phenolic allyl compounds as precursors for the whole group; they themselves are formed by an alkylation process involving cinnamyl pyrophosphate (C₉) and a phenolic (C₆) unit. The allyl phenols then undergo oxidation to dalbergenones and further cyclisation and oxidation lead to 4-phenyl coumarins. They considered³ Claisen migration as a laboratory analogy for this coupling process; the unsuitability of this analogy has already been pointed out.⁴ Moreover for phenolic precursors of dalbergenones with methoxyl (or hydroxyl) groups in ring 'B', this alkylation process would not be facile.

In an earlier publication⁴ from this laboratory an alternative pathway to the neoflavanoids was suggested in which 4-phenyl coumarins were postulated as precursors of the whole group. According to this scheme the 4-phenyl coumarins undergo reduction to the corresponding cinnamyl alcohols and these, having the oxygen functions both at ortho and para positions in ring (A), are in a favourable position to undergo reduction in the side chain leading to latifolin type of skeleton. Subsequent oxidation gives rise to dalbergenones. This is more in accordance with the idea of Birch⁵ regarding the origin of natural allyl phenols from cinnamyl alcohols.

In this preliminary publication we wish to report laboratory experiments in support of the above idea. 7-Methoxy-4-phenyl coumarin⁶ (III) was reduced by the inverse-addition of lithium aluminium hydride in dry ether to 3-

(2-hydroxy-4-methoxyphenyl)-3-phenyl allyl alcohol (IV a). It crystallised from hot benzene as colourless prisms, m.p. 140–41° (Found: C, 74.3; H, 5.9. C₁₆H₁₆O₃ requires C, 74.7; H, 6.2%). $\lambda_{\text{max}}^{\text{MeOH}}$ 240 m μ with inflexion at 285 m μ . Catalytic hydrogenation gave the corresponding propyl alcohol as an oil, $\lambda_{\text{max}}^{\text{MeOH}}$ 280 m μ . Methylation of (IV a) by methyl iodide, acetone-potassium carbonate method followed by purification on silica gel gave the methyl ether (IV b). It was obtained as colourless plates from methanol, m.p. 68–70° (Found: C, 75.1; H, 6.8. C₁₇H₁₈O₃ requires C, 75.5; H, 6.7%). $\lambda_{\text{max}}^{\text{MeOH}}$ 240 and 280 m μ . A small amount of (IV b) gave on oxidation with Lemieux reagent⁷ 2,4-dimethoxy benzophenone identical with an authentic compound.

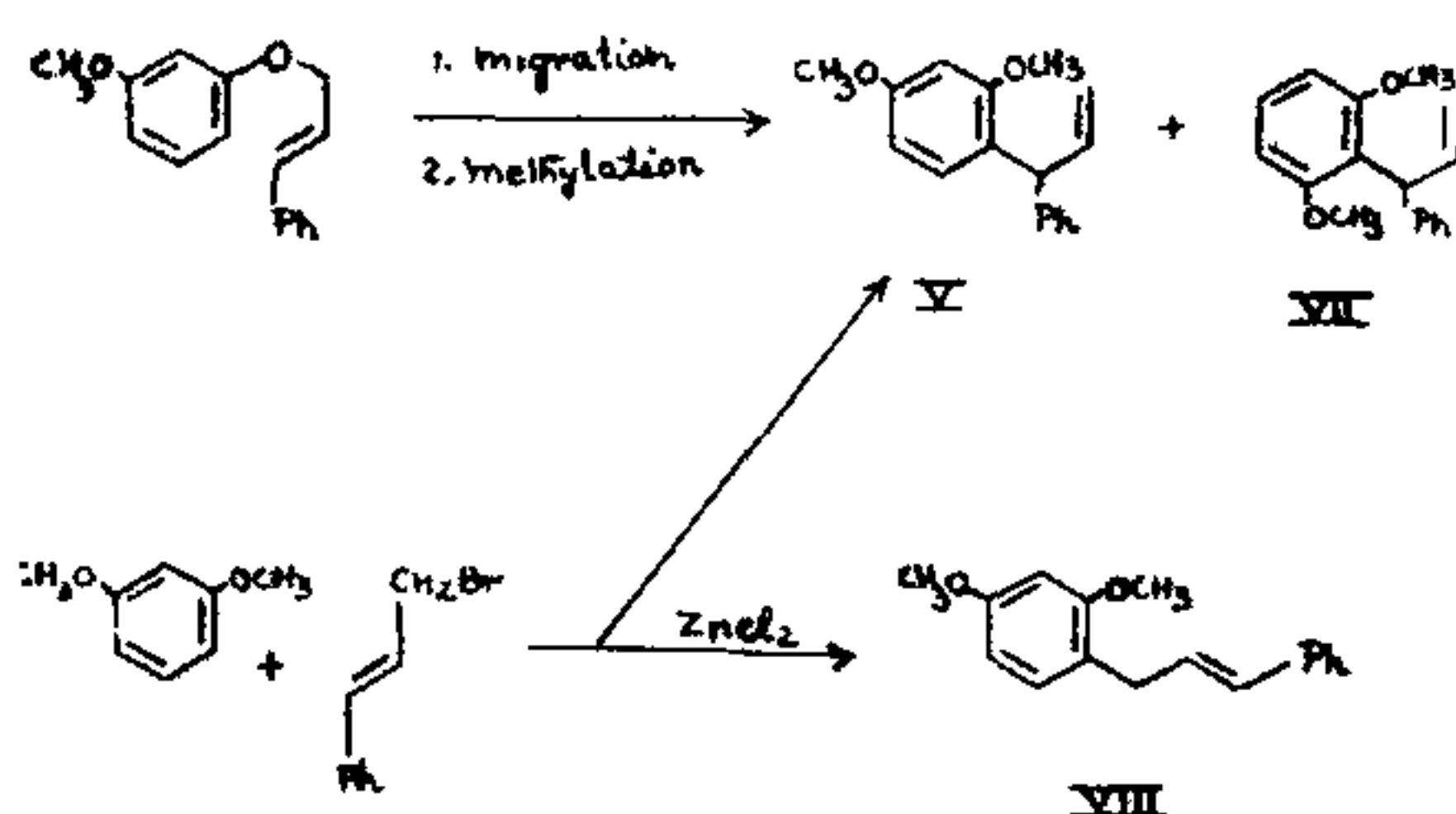
The methoxy cinnamyl alcohol (IV b) when stirred at room temperature for one hour with previously prepared mixture of aluminium chloride and lithium aluminium hydride, produced a (1:1) mixture of 3- (2:4-dimethoxy phenyl)-3-phenyl propene (V) and the corresponding 1:1-disubstituted isomer (VI). Comparison with authentic allyl (V) and propenyl (VI) compounds established their



identity and the composition of the mixture was determined approximately by visual estimation of colour in spots produced on T.L.C. plates. Variation of the ratio of aluminium chloride to the hydride (1 to 3 moles of AlCl₃ per mole of LAH) and variation of reaction temperature did not appreciably alter the composition of the mixture. Fused zinc chloride can substitute aluminium chloride in this reaction. The cationic intermediate produced with this reagent is stable as shown in one experiment in which the cinnamyl alcohol (IV b) was treated first with zinc chloride and the hydride was added subsequently to the mixture;

the composition of the product was essentially the same as when previously mixed reagents were employed. However, the use of zinc chloride leads to the formation of more of isomer (VI) (70%).

Authentic diphenyl allyl compound (V) was prepared by methylation of 3-(2-hydroxy-4-methoxyphenyl)-3-phenyl propene.³ It was also



obtained by coupling resorcinol dimethyl ether with cinnamyl bromide in the presence of zinc chloride. This reaction gave a complicated mixture of eight compounds; out of these two major and closely moving compounds were separated. They consisted of the allyl compound (V) and the isomeric benzyl styrene (VIII) and were used to identify the product obtained by the Claisen migration route which was contaminated with 3-(2, 6-dimethoxy-

phenyl)-3-phenyl propene (VII). The allyl compound (V) was a liquid; $\lambda_{\text{max}}^{\text{MeOH}}$ 285 μ (Found: C, 80.5; H, 7.6. $\text{C}_{17}\text{H}_{18}\text{O}_2$ requires C, 80.0; H, 7.1%).

Authentic propenyl isomer (VI) was prepared by Grignard reaction of 2, 4-dimethoxy benzo-phenone with ethyl magnesium bromide and dehydrating the product. It crystallised from methanol as colourless plates, m.p. 73–74° (Found: C, 79.5; H, 7.6. $\text{C}_{17}\text{H}_{18}\text{O}_2$ requires C, 80.0; H, 7.1%). $\lambda_{\text{max}}^{\text{MeOH}}$ 240 m μ with inflexion at 285 m μ .

Fuller scope of this reaction is under investigation.

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THIN LAYER CHROMATOGRAPHY OF INORGANIC IONS

Part I. Separation of Zinc, Copper, Cadmium, Cobalt and Nickel as their Thiocyanate Complexes

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THE technique of Thin Layer Chromatography (T.L.C.), on account of its speed and elegance, has been extensively employed for organic separations. Seiler¹ et al., in a series of papers, have attempted to apply this technique to inorganic ions but on repeating some of these experiments, no compact spots were obtained. Hranisavljevic—Jakovljevic² et al. also described separation of metals as their dithizonates. Apart from this no extended use appears to have been made of this technique for the separation of inorganic ions.

Following the suggestions of Pollard and McComie³ that the solubility of metallic thiocyanate in organic solvents should merit their examinations in chromatography, paper chromatographic methods were developed in this laboratory, for the separation from their mixture of (1) copper, cobalt and nickel⁴ and

(2) cadmium and zinc.⁵ It was considered desirable to extend these investigations to explore the possibility of the separation of all the above five ions from their mixture by using T.L.C.

It is well known that of the five above mentioned ions, Cobalt and Zinc thiocyanates are fairly soluble in organic solvents. However, on addition of Pyridine, all the five of the metal ions form complexes of the type $\text{M Py}_n (\text{SCN})_m$, which are extractable with organic solvents. The combination of solvents, and (i) Thiocyanate or (ii) Pyridine and thiocyanate in the same solution, however, gives an eluent which effectively buffers the chromatogram and thus become more effective for the chromatographic separations.

In the present investigation several eluents based on thiocyanate with or without pyridine