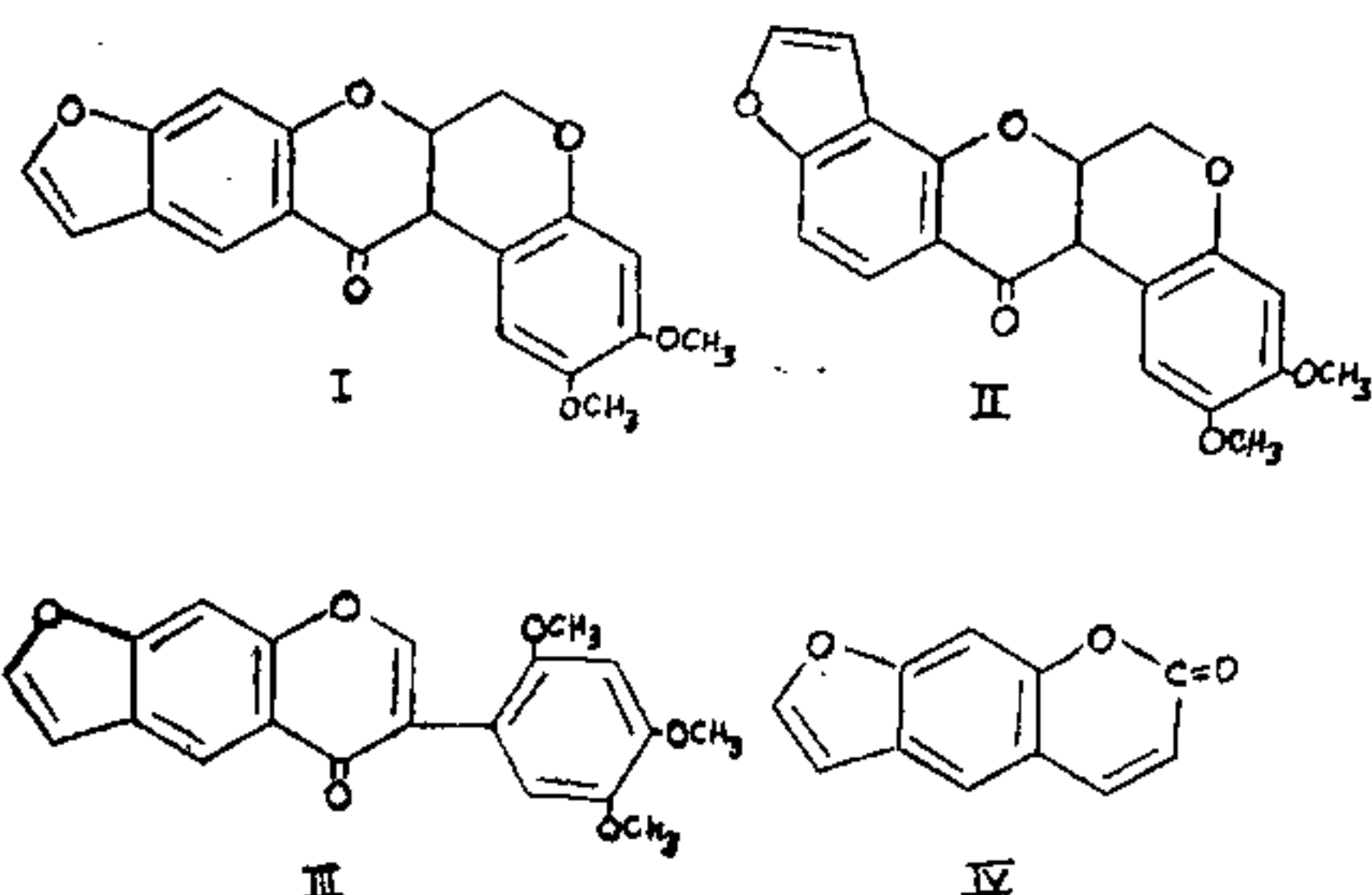


A NEW SYNTHESIS OF ISOELLIPTOLISOFLAVONE AND SYNTHESIS OF ISOELLIPTIC ACID

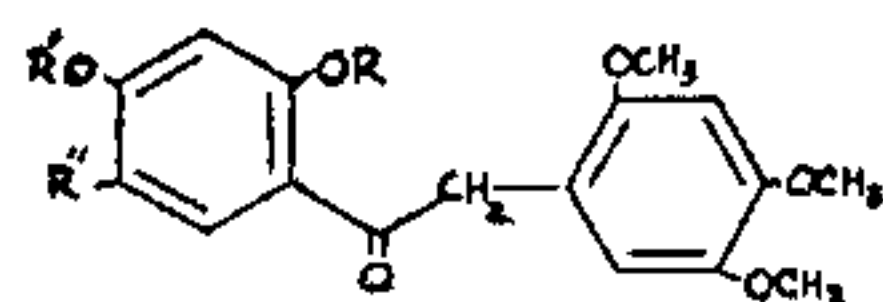
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IN an earlier publication¹ a new approach to the synthesis of rotenoids was described and was illustrated by the synthesis of munduserone and elliptone. Erosone, isolated as a minor component from the seeds of *Pachyrrhizus erosus* (yam beans), has been suggested² the structure (I) which is closely related to that of elliptone (II) and is its linear isomer. The key intermediate required for its synthesis is isoelliptolisoflavone (III). The synthesis of a furanoisoflavone of this type is not possible from a 7-hydroxyisoflavone because the methods available for the construction of a furan ring on it lead only to the synthesis of an angularly fused compound. Therefore, we have now used the procedure adopted by Seshadri and Sood³ for the synthesis of psoralen (IV) in which the required migration of an allyl group is effected in the ketone stage itself as described below.



lead only to the synthesis of an angularly fused oxyphenyl-2, 4, 5-trimethoxybenzylketone (V)¹ was the starting point. It was methylated to (VI), m.p. 105–106°, and subjected to Claisen migration. The allyl group migrates to the position para to methoxyl to yield the 5-allyl-

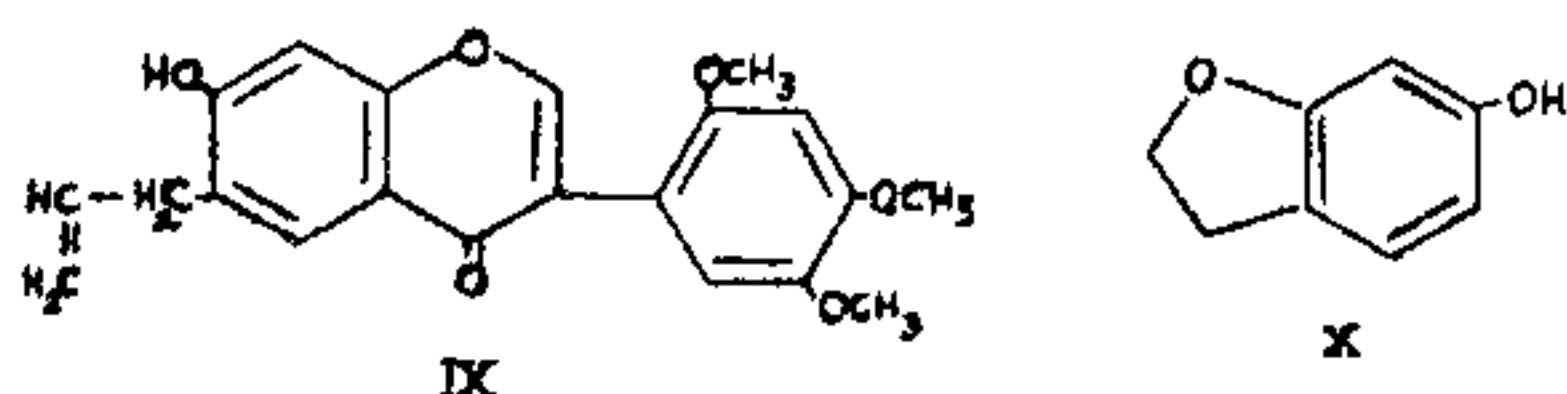


V, $R=R'=H$; $R''=Allyl$

VI, $R=CH_3$; $R'=Allyl$; $R''=H$

VII, $R=CH_3$; $R'=H$; $R''=Allyl$

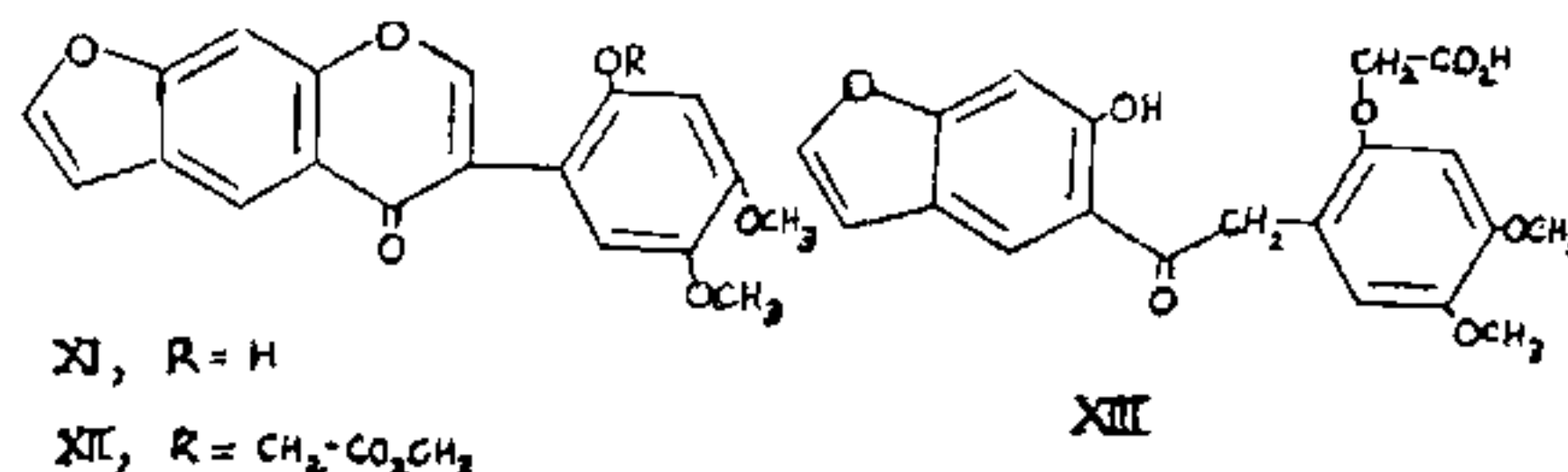
VIII, $R=R'=H$; $R''=Allyl$



desoxybenzoin (VII), m.p. 146–147°. Subsequent partial demethylation with aluminium chloride

in acetonitrile yielded the ketone (VIII), m.p. 170–171°, which underwent cyclisation to form 7-hydroxy-6-allyl-2', 4', 5'-trimethoxyisoflavone (IX), m.p. 262°. On treatment with osmium tetroxide followed by sodium metaperiodate and subsequent ring closure with polyphosphoric acid it gave isoelliptolisoflavone, m.p. 191°, which was found to be identical (mixed m.p. and U.V. spectra) with an authentic sample supplied by Dr. Fukui who obtained it by a different route starting from (X).⁴ The present method is far more convenient.

Isoelliptolisoflavone smoothly underwent partial demethylation at the 2'-position with aluminium chloride in acetonitrile to yield the 2'-hydroxy compound (XI), m.p. 200–201°, which on refluxing with bromoacetic ester in acetone solution in the presence of potassium carbonate gave the 2'-carbomethoxymethoxyisoflavone (XII), m.p. 138–140°. This intermediate on alkaline degradation opened the oxygen ring and gave isoelliptic acid (XIII), m.p. 193–194°.



The melting point of the synthetic acid is different from that reported (204°) for the acid obtained by the degradation of dehydroerosone. A direct comparison with an authentic sample was not possible since it is not obtainable from any of those who handled erosone. Therefore, yam beans (500 g.) obtained from Calcutta were extracted to isolate erosone which could be degraded to the desired acid. The sample, however, did not yield erosone; four other compounds were obtained. Three of these were major components and were identified as pachyrrhizin, erosin and dehydroneotenone; the fourth was very small and appeared to be dolineone. Further work on fresh samples of beans and on the conversion of isoelliptic acid into the rotenoid are in progress.

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