A Possible Chemical Analogy for Pterocarpan Biosynthesis

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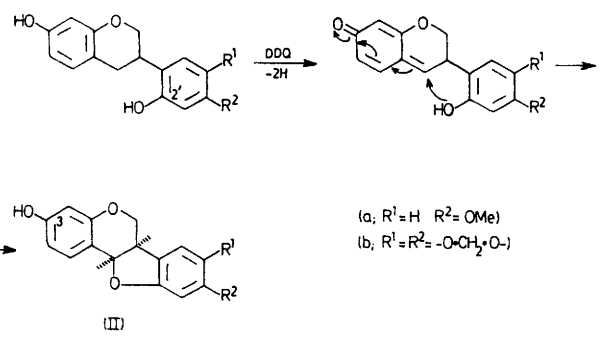
Summary Oxidative conversion of 2'-hydroxyisoflavans to pterocarpans by 2,3-dichloro-5,6-dicyanobenzoquinone is suggested as a possible chemical analogy for the corresponding biosynthetic pathway.

ALTHOUGH the biogenesis of flavonoids has been well studied[1] direct experimental evidence for the interconversion *in vivo* of different classes of isoflavonoids is available only in a few cases.[2] In particular, there is no evidence for the interconversion of pterocarpans and isoflavans. On the



basis of the characteristic 2′-hydroxylation pattern of natural isoflavans and their chemical analogues, it could be suggested that isoflavans are derived by reductive ring-opening of pterocarpans.[2] On the other hand, Grisebach and his co-workers[3] have shown that 2′-hydroxylation of an isoflavone or isoflavanone is a step in the biosynthesis of coumestans.

We now report a new chemical correlation that could suggest that the conversion of 2′-hydroxyisoflavans to pterocarpans might also occur *in vivo*. Mild oxidation of the isoflavans (Ia) or (Ib) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene at room temperature for 8 h afforded demethylhomopterocarpin (IIa) or maackiain (IIb) in 30% yield (n.m.r., direct t.l.c. comparison). The reaction most probably proceeds through a quinonemethide intermediate, which undergoes a nucleophilic addition by the 2′-OH group. Similar behaviour shown by 2,4′-dihydroxydiphenylethane[4] and 2,2′-dihydroxydiphenylethane[5] supports this hypothesis. The 3-OH (or 3-OR) substitution in all the natural pterocarpans so far found in Nature is consistent with the suggested biosynthetic pathway, which requires such an activating group.

Shortage of starting materials (prepared by hydrogenation of the corresponding (II), extracted from *Swartzia madagascariensis* heartwood[6]) prevented a closer investigation of possible minor products of the reaction. However, the ready further oxidation of (II) to coumestans has been already demonstrated by Grisebach,[7] and Roux[8] and their co-workers.

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