A New Route to Chromanocoumarans. Synthesis of (±)-Pterocarpin

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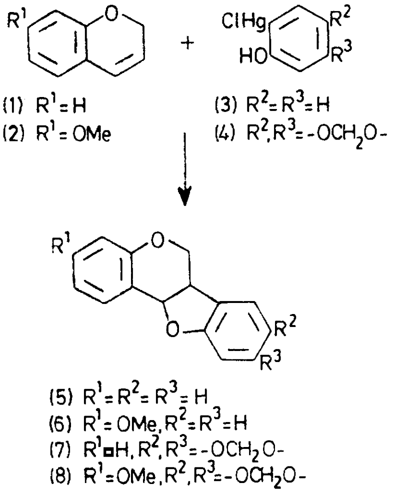
Summary (±)-Pterocarpin (**8**) and other chromanocoumarans were synthesized in one step by the reaction of 2*H*-chromens with *o*-chloromercuriphenols in the presence of lithium chloropalladite.

The naturally occurring chromanocoumarans, pterocarpans, have usually been synthesized by acid-catalysed cyclization of 2′-hydroxyisoflavanols.[1] However, it is not easy to prepare 2′-hydroxyisoflavanols substituted with hydroxy-, methoxy-, or methylenedioxy-groups in the same positions of the A and D rings as in the naturally occurring pterocarpans.



In Heck arylation with phenylpalladium chloride in protic solvents, we have found that a phenyl group and the anion part of a protic solvent add simultaneously to the double bond of benzocycloalkenes.[2] We present here a new synthesis of chromanocoumaran derivatives, applying this oxyphenylation to 2*H*-chromens by the use of phenolic palladium complexes.

In the presence of Li_2PdCl_4 the reaction of 2*H*-chromen (**1**) with *o*-chloromercuriphenol (**3**) in acetonitrile at room temperature gave the chromanocoumaran† (**5**),[3] m.p. 125—127 °C, in 85% yield. Compound (**5**) was also formed in acetone (78%) and in acetic acid (68%). The product of the reaction of 7-methoxy-2*H*-chromen (**2**) with (**3**) and Li_2PdCl_4 in acetic acid solution gave the 7-methoxychromanocoumaran† (**6**),[4] m.p. 94–95 °C in 54% yield, after chromatography on silica gel.

Compound (**4**) was prepared by the reaction of 3,4-methylenedioxyphenol with mercury(II) acetate in methanol below 10 °C followed by treatment with sodium chloride. The ^1H n.m.r. spectrum of (**4**) [$(CD_3)_2SO$, δ 6·4 (1H, s) and 6·8 (1H, s)] indicated the presence of two isolated aromatic protons. Demethoxypterocarpin† (**7**), m.p. 180—181 °C, was obtained by the reaction of (**1**) with (**4**) and Li_2PdCl_4 in acetic acid (36%): δ ($CDCl_3$); 3·62 (2H, d, *J* 9 Hz), 4·26 (1H, m), 5·46 (1H, d, *J* 6 Hz, 4-H), 5·88 (2H, s, OCH_2O), and 6·87–7·53 (6H, m, ArH).

The reaction of (**2**) with (**4**) and Li_2PdCl_4 in acetone and subsequent chromatography on silica gel afforded (±)-pterocarpin† (**8**),[5] m.p. 184—185 °C, in 58% yield, the i.r. and ^1H n.m.r. spectra of which are identical with those of an authentic sample.[6]

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† All the products described in this report gave satisfactory elemental analysis.

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