

Synthesis of the Carbazole Alkaloid Murrayaquinone-B

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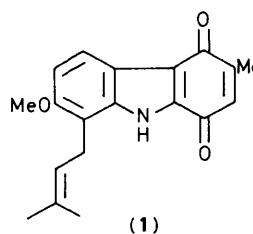
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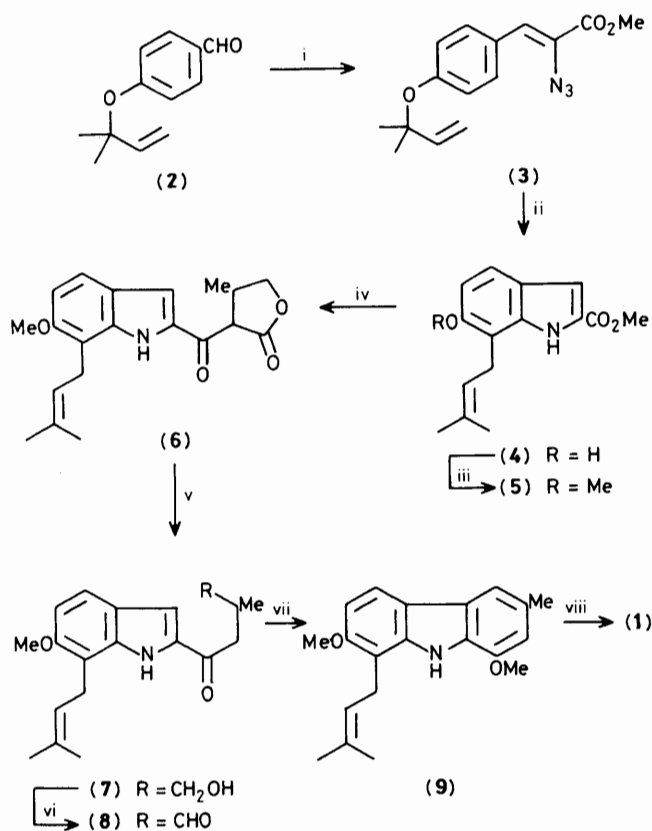
A short synthesis of the novel carbazolequinone alkaloid murrayaquinone-B (**1**), based on a regioselective Claisen rearrangement to give the indole (**4**) followed by a new method of benzannulation of indoles, is described.

The plants of the genus *Murraya* (Rutaceae) are the major source of carbazole alkaloids,¹ and recently the first example of a naturally occurring carbazolequinone, murrayaquinone-B (**1**), has been isolated from the root bark of *M. euchrestifolia* Hayata.² In continuation of our interest in heterocyclic quinones from natural sources,³ we now report the first synthesis of this novel carbazole alkaloid (**1**).

The overall strategy involves, as key steps, the facile formation of the indole (**4**) by sequential indolisation and regioselective Claisen rearrangement,⁴ followed by annulation of the third ring employing a new method⁵ for the conversion of indoles into carbazoles. 4-(1,1-Dimethylallyloxy)benzaldehyde (**2**) was condensed³ with methyl azidoacetate to give the azidocinnamate (**3**) (86%). On heating

the azide (**3**) in toluene for 3 h, concomitant indole formation and regioselective Claisen rearrangement occurred to give the 6-methoxyindole (**4**) (53%), which was converted into the corresponding 6-methoxyindole (**5**), m.p. 142—143 °C, by





Scheme 1. Reagents: i, MeO₂CCH₂N₃, NaOMe, MeOH, -15 °C; ii, toluene, reflux; iii, MeI, K₂CO₃, acetone; iv, 4-methylbutyrolactone, NaOMe, dioxane; v, H₂O, NaOH, dioxane; vi, PCC, CH₂Cl₂; vii, MeOH-BF₃; viii, hv, air, MeOH.

treatment with iodomethane and potassium carbonate in acetone.

The remaining carbon atoms required for the annelation of the third ring were added by a simple Claisen condensation^{5,7} of the indole ester (**5**) with 4-methylbutyrolactone to give the lactone (**6**) (66%), which on heating in aqueous dioxane containing a trace of sodium hydroxide underwent hydrolysis and decarboxylation to give the alcohol (**7**) (85%), m.p. 79–80 °C. Reaction of the alcohol (**7**) with pyridinium chlorochromate (PCC) gave the corresponding aldehyde (**8**) (84%) which was cyclised (46%) to give 1,7-dimethoxy-3-methyl-8-(3-methylbut-2-enyl)-9*H*-carbazole (**9**), m.p. 103–105 °C, by stirring in boron trifluoride–methanol complex for 17 h at room temperature. Photo-oxidation of the 1-methoxy-carbazole (**9**) by irradiation of an aerated methanol solution for 60 min gave murrayaquinone-B (**1**), albeit in low yield, whose spectral properties were identical to those of the natural product.

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