

The following general procedure as exemplified for the synthesis of 5-(2-oxo-3-indolinylidene)-3-benzyl-2-(1-naphthylimino)-4-thiazolidinone was adopted for the preparation of all the thioindigoid dyes.

A mixture of 3-benzyl-2-(1-naphthylimino)-4-thiazolidinone (3.32g, 0.01 mole), isatin (1.5g, 0.01 mole), anhydrous sodium acetate (3.2g, 0.04 mole), glacial acetic acid (40 ml) and acetic anhydride (4ml) were refluxed for about 4.5 hrs. After cooling the reaction mixture was poured into cold water when a red precipitate was formed. The precipitate was filtered, washed successively with hot water, dilute acetic acid and finally several times with ethanol and dried.

The IR spectrum (nujol) showed characteristic peaks at 3200 cm^{-1} (NH); $2950, 2880\text{ cm}^{-1}$ (CH_2); $1740, 1720\text{ cm}^{-1}$ ($\text{C}=\text{O}$); 1650 cm^{-1} (aliphatic $\text{C}=\text{C}$); 1615 cm^{-1} ($\text{C}=\text{N}$); $1596, 1480\text{ cm}^{-1}$ (aromatic $\text{C}=\text{C}$) and 740 cm^{-1} ($\text{C}-\text{S}$).

All of them showed consistent elemental analysis.

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A New Synthesis of Murrayacinine

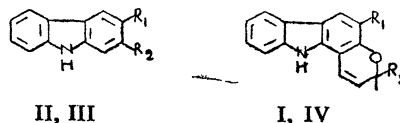
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In a previous communication, we reported the structure and synthesis of murrayacinine (I), a carbazole alkaloid isolated from the stem-bark of *Murraya koenigii* Spreng. The synthesis involved condensation of citral with 2-hydroxy-3-formyl carbazole (II) which in turn was obtained by chromic acid oxidation of 2-hydroxy-3-methyl carbazole (III). In consideration of the relatively poor yield of the alkaloid obtained in our previous synthesis and in view of the fact that murrayacinine (I) is an oxidative variant of the alkaloid mahanimbine (IV)², a facile conversion

of IV to I was achieved by the use of DDQ (dichloro-dicyano benzoquinone), a reagent that has recently been used³⁻⁵ for similar oxidation of aromatic methyl groups to corresponding formyl groups. Mahanimbine in dry benzene was stirred with DDQ at room temperature for 2 hours. The product was then taken in ether, washed with 1% NaOH and water. From the reaction mixture murrayacinine was isolated by preparative thin layer method.



- (I) $\text{R}_1 = -\text{CHO}$; $\text{R}_2 = \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}=\text{C} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$
- (II) $\text{R}_1 = -\text{CHO}$; $\text{R}_2 = -\text{OH}$
- (III) $\text{R}_1 = -\text{CH}_3$; $\text{R}_2 = -\text{OH}$
- (IV) $\text{R}_1 = -\text{CH}_3$; $\text{R}_2 = \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}=\text{C} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$

Experimental

Mahanimbine (50 mg) in dry benzene (10 ml) was stirred and a solution of DDQ in dry benzene (molar proportion) was added to it over a period of 15 minutes. The stirring was continued for 1 hour at room temperature. The reaction product was then treated with 1% NaOH and extracted with ether. The ether solution was washed with water to free it from alkali and dried over sodium sulphate.

After the removal of the ether the residue was taken in benzene and subjected to preparative t. l. c. The spot identical with natural murrayacinine was scraped out from the t.l.c. plate, extracted with alcohol and filtered. The solid obtained on evaporation of the alcohol was purified and recrystallised from benzene-petroleum ether mixture. The compound was finally identified as murrayacinine (yield 15 mg) by a direct comparison with a pure specimen of the sample (uv, ir, m.p., m.m.p., t.l.c.). The other constituents in the chromatogram was not characterised due to poor yield.

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