

THE REACTION OF 3-HYDROXYCOUMARIN WITH BENZALACETONE

V.K. Ahluwalia*, Keya Mukherjee & Nimmi Rani

Department of Chemistry, University of Delhi, Delhi-110007, India

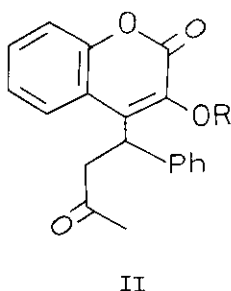
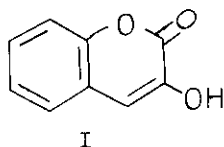
Abstract - The reaction of 3-hydroxycoumarin (I) with benzalacetone in presence of dioxane - piperidine afforded 3-hydroxy-4-(α -phenyl- β -acetylethyl)coumarin (IIa) which on acetylation with Ac_2O /pyridine gave a cyclised product, 2-acetoxy-2-methyl-4-phenyl-10-oxo-3,4-dihydropyrano[2,3-c][1]benzopyran (III).

In view of the interesting results obtained in the reaction of 4-hydroxycoumarin with benzalacetone¹, which gave warfarin² [4-hydroxy-3-(α -phenyl- β -acetylethyl)coumarin], a well known anticoagulant rodenticide^{3,4} and in view of the inhibiting effect of 3-hydroxycoumarin on the growth of avena roots⁵, a study of the reaction of 3-hydroxycoumarin⁶ (I) with benzalacetone has been carried out. This study is of special importance in view of the special properties of 3-hydroxycoumarins⁷⁻¹⁰.

Thus, the reaction of 3-hydroxycoumarin (1 g) with benzalacetone (1 ml) in dioxane (5 ml) by refluxing in presence of piperidine (1-2 drops) for 48 h at 120-130° gave a crystalline product A (0.6 g), $\text{C}_{19}\text{H}_{16}\text{O}_4$, m.p. 166-167°. It was isolated from the reaction mixture by extraction with sodium carbonate solution which removed the unreacted 3-hydroxycoumarin, followed by extraction with sodium hydroxide (2%) and acidification of the alkaline extract. The product A gave green colour with alcoholic ferric chloride. In the IR(KBr) spectrum of the compound, two bands at 1700 cm^{-1} and 1720 cm^{-1} indicated the presence of two carbonyl groups while band at 3500 cm^{-1} showed the presence of a hydroxyl group. The structure of the compound was finally established on the basis of the NMR spectral data of its methyl ether which showed besides other signals the presence of an acetyl group as a singlet at δ 2.12, a doublet centred at δ 3.50 ($J=6\text{ Hz}$) integrating for two protons (could be assigned to the methylene proton) and a triplet centred at δ 5.20 ($J=6\text{ Hz}$) integrating for one proton (methine proton).

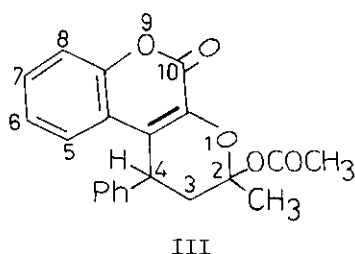
* Author to whom all correspondence be made.

On the basis of the above spectral data, compound A could be assigned the structure 3-hydroxy-4-(α -phenyl- β -acetylethyl)coumarin (IIa) and its methyl ether as 3-methoxy-4-(α -phenyl- β -acetylethyl) coumarin (IIb),



a, R = H

b, R = CH₃



However, acetylation of IIa in refluxing acetic anhydride and pyridine gave a compound, which in its NMR spectrum showed a singlet at δ 2.28 for the acetoxy group, a double doublet centred at δ 3.36 ($J=6$ Hz, 17 Hz) integrating for two protons (methylene proton) and a triplet at δ 5.28 ($J=6$ Hz) equivalent to one proton for C₄ in addition to a multiplet at δ 7.30 corresponding to 9 protons in all. The above spectral data led us to assign the structure 2-acetoxy-2-methyl-4-phenyl-10-oxo-3,4-dihydropyran [2,3-c][1]benzopyran (III) to the product obtained by the acetylation of IIa.

The results obtained are different from the reaction¹⁰ of 3-hydroxy-coumarin with chalcone in which a cyclic compound is directly obtained. However, in the present reaction, the product A, an open chain compound is obtained which can be cyclised to the closed chain compound during acetylation. It is believed that the reaction follows the same course as postulated¹⁰ earlier.

All compounds analysed well for C & H.

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