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REACTIONS OF NITRILES VI. SYNTHESIS OF LINEAR AND ANGULAR PYRONOCHROMANONES

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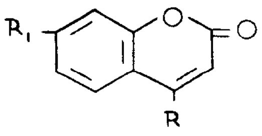
The present communication describes the cyanoethylation of 7-hydroxy and 7-hydroxy-4-methylcoumarins which has so far not been investigated and provides a convenient method for the synthesis of some naturally occurring pyronochromanones such as clausenin and clausenidin[1].



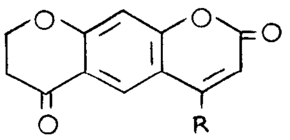
I

a) R = H ; R_1 = OCH_2CH_2CN

b) R = H ; R_1 = OCH_2CH_2COOH

c) R = CH_3 ; R_1 = OCH_2CH_2CN

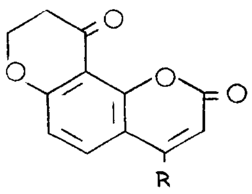
d) R = CH_3 ; R_1 = OCH_2CH_2COOH



II

a) R = H

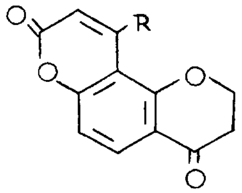
b) R_1 = CH_3



III

a) R = H

b) R = CH_3



IV

a) R = H

b) R = CH_3

Spectroscopic and analytical evidence for all new compounds are compatible with the structures given.

7-Hydroxycoumarin when refluxed with acrylonitrile in the presence of aqueous alkali with dioxane as solvent afforded the nitrile Ia, $C_{12}H_9NO_3$, m.p. 167-69° which was hydrolysed to the acid Ib, $C_{12}H_{10}O_5$, m.p. 164-66°. The acid Ib on cyclisation with polyphosphoric acid afforded a mixture of pyronochromanones which were separated by chromatography. Elution with benzene gave the isomer IIa, $C_{12}H_8O_4$, m.p. 207-09° (2,4DNP, m.p. 291-92° decomp.). The fraction eluting from benzene-ether (1:1) was the isomer IIIa, $C_{12}H_8O_4$, m.p. 217-19° (2,4DNP, m.p. 286-88° decomp.).

An attempt to synthesise IIa from 7-hydroxychromanone by a Pechmann condensation with malic acid in the presence of sulphuric acid led to the formation of a pyronochromanone $C_{12}H_8O_4$, m.p. 201-03°, which was different from the two isomers obtained above (m.m.p.) and hence must have the only other possible structure IVa.

The corresponding 4-methyl compounds were prepared by an analogous route from 7-hydroxy-4-methylcoumarin. Ic, m.p. 128-30°; Id, m.p.197-99°; IIb, 235-37° (2,4DNP, m.p. 297-98° decomp.); IIIb, m.p. 244-46° (2,4DNP, m.p. 292° decomp.). The structure IIb was assigned on the basis of an alternative synthesis. Pechmann condensation of 7-hydroxychromanone with ethyl acetoacetate in the presence of dry nitrobenzene could afford the pyronochromanones IIb and IVb. In the actual working of the reaction, only one pyronochromanone m.p. 234-35° was obtained. That the above synthesised pyronochromanones was identical with the linear isomer obtained before was established by a mixed m.p. (which was not depressed) as well as by the observation that it was different from the pyronochromanone IVb[2].

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References :

1. B. S. Joshi, V. N. Kamat and A. K. Saksena, Tetrahedron, 23, 4777 (1967).
2. J. R. Merchant and J. R. Patell, J. Chem. Soc., (C) 1544 (1969).