

**SYNTHESIS OF
γ-PYRONOCHROMANONES**

IN our previous communications¹⁻⁴ we have reported that the cyanoethylation of hydroxycoumarin derivatives followed by hydrolysis and cyclisation affords a convenient method for the synthesis of linear and angular α-pyronechromanones. The present communication describes the synthesis of γ-pyronechromanones by the application of cyanoethylation on hydroxy chromone, flavone and isoflavone derivatives.

7-Hydroxy-2-methylchromone when reacted with acrylonitrile in the presence of alkali afforded the nitrile Ia, m.p. 152-54° (Found C, 68.4; H, 5.0; N, 6.3 Calcd. for C₁₃H₁₁O₃N; C, 68.2; H, 4.8; N, 6.5%) which was hydrolysed to the corresponding propionic acid Ib, m.p. 169-71° (Found C, 63.1; H, 5.1 Calcd. for C₁₃H₁₂O₅; C, 62.9; H, 4.9%). The latter on cyclisation afforded only one compound (TLC) m.p. 183-85° (Found C, 67.3; H, 4.7 Calcd. for C₁₃H₁₀O₄; C, 67.8; H, 4.3%) which on the basis of the n.m.r. spectrum was assigned the angular structure IIa. The protons H_a and H_b were identified as doublets (δ CHCl₃, 6.95 and 8.25, J = 9 cps). It gave a 2,4-dinitrophenylhydrazone m.p. 286-88° (Found: N, 14.1 Calcd. for C₁₉H₁₄N₄O₇; N, 13.7%).

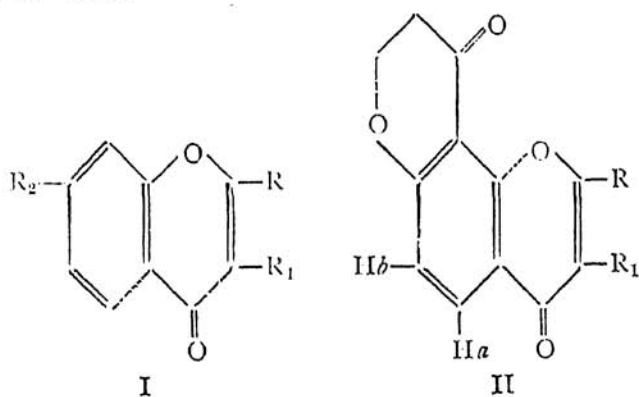
C₁₈H₁₂O₄; C, 74.0; H, 4.1%) as indicated by its n.m.r. spectrum. The protons H_a and H_b were identified as doublets (δ CDCl₃, 6.98 and 8.22, J = 9 cps). It gave a 2,4-dinitrophenylhydrazone, m.p. 265-67° (Found N, 11.9 Calcd. for C₂₄H₁₆N₄O₇; N, 11.9%).

7-Hydroxy-2-methylisoflavone (nitrile Ie, m.p. 144-46°; (Found C, 74.1; H, 4.9 Calcd. for C₁₉H₁₅O₃N; C, 74.6; H, 4.9%; acid If, m.p. 182-84°; Found C, 70.5; H, 5.0 Calcd. for C₁₉H₁₆O₅ C, 70.4; H, 4.9%) also gave only IIc, m.p. 184-86° (TLC) (Found C, 74.5; H, 5.0 Calcd. for C₁₉H₁₄O₄; C, 74.5; H, 4.5%) whose structure was confirmed by its n.m.r. spectrum which showed the protons H_a and H_b as doublets (δ CDCl₃, 6.93 and 8.28, J = 9 cps). Its 2,4-dinitrophenylhydrazone melted at 268-70° (Found N, 11.3 Calcd. for C₂₅H₁₉O₇N₄; N, 11.5%).

It is interesting to note that whilst 7-hydroxycoumarin derivatives gave both the linear and the angular chromanones, in the case of the chromone and flavones only the angular derivative is obtained.

The cyanoethylation of 5-hydroxy-2-methylchromone and 5-hydroxyflavone failed to occur even under drastic conditions and the original compound was recovered unchanged. This is probably due to the hydrogen-bonding between the hydroxyl and the carbonyl groups which is also reported⁵ to inhibit other reactions such as methylation.

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	R	R ₁	R ₂		R	R ₁
(a)	CH ₃	H	O (CH ₂) ₂ CN	(a)	CH ₃	H
(b)	CH ₃	H	O (CH ₂) ₂ CO ₂ H	(b)	Ph	H
(c)	Ph	H	O (CH ₂) ₂ CN	(c)	CH ₃	Ph
(d)	Ph	H	O (CH ₂) ₂ CO ₂ H			
(e)	CH ₃	Ph	O (CH ₂) ₂ CN			
(f)	CH ₃	Ph	O (CH ₂) ₂ CO ₂ H			

Similarly, 7-hydroxyflavone (nitrile Ic, m.p. 135-37°; Found C, 74.0; H, 4.7; N, 4.9 Calcd. for C₁₈H₁₃O₃N; C, 74.2; H, 4.5; N, 4.8%); acid Id, m.p. 247-49°; Found C, 69.2; H, 4.8 Calcd. for C₁₈H₁₄O₅; C, 69.7; H, 4.5%) also yielded only the angular chromanone IIb, m.p. 218-20° (Found C, 74.0; H, 4.2 Calcd. for

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4. —, — and Mrs. Barve, N. V., *J. Indian Chem. Soc.* (under print).
5. Elderfield, R. C., *Heterocyclic Compounds*, Vol. II, John Wiley & Sons, Inc., 1951, p 265.