Synthesis of Some New 2,2-Dimethylchromens Related to Phloroglucinol

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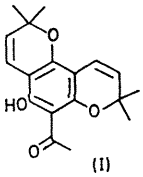
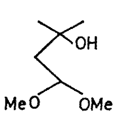
Summary Pyridine or pyridinium hydrochloride catalysed condensation of 3-hydroxyisovaleraldehyde dimethyl acetal with phloroacetophenone gave six characterisable products all containing the 2,2-dimethylchromen ring system, including the tricyclic pyranochromen (I).

THE direct synthesis of 2,2-dimethylchromens from phenols using 3-hydroxyisovaleraldehyde dimethyl acetal has been reported by Crombie *et al.*[1] Previous applications of this and related reactions[2] have resulted in the formation of only one pyran ring system per phenolic nucleus and cyclisation to the chromen appears to have taken place exclusively on non-chelated hydroxy-groups. We now report the synthesis of (I) in which a second dimethylpyran ring is cyclised on to a chelated hydroxy-group of phloroacetophenone.



(I)



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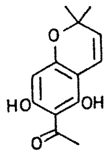

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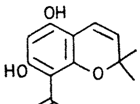

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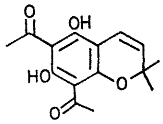
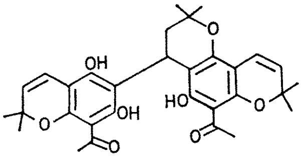
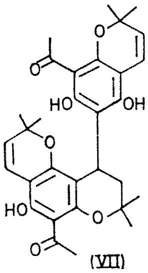


(V)



(VI)



(VII)

Condensation of an excess of 3-hydroxyisovaleraldehyde dimethyl acetal (II) with phloroacetophenone in the presence of pyridine at 150°[3] gave, after chromatography, (I) (4·1%) m.p. 87—90°, λ_{max} 269·5 nm, which was hydrogenated to the known tetrahydropyranochroman m.p. 118° (lit.[4] 117—118°). An inseparable mixture of the isomeric chromens (III) and (IV) (2·8%) was also obtained which on hydrogenation and separation gave the corresponding chromans, indistinguishable from authentic synthetic samples.[5]

Secondary products isolated from the reaction mixture included the diacetylchromen (V), m.p. 138—139°, λ_{max} 270 nm, (1·8%), formed subsequently to disproportionation of phloroacetophenone, and the unsymmetrical dimers (VI), m.p. 200—202·5°, M^+ 534, and (VII), m.p. 190—192°, M^+ 534 (2·1%), presumably derived by protonation of (I) followed by carbonium-ion attack on (IV).

The yields of (I) were poor when the reaction was catalysed by pyridine, but in the additional presence of pyridinium hydrochloride substantial improvement was obtained, (I) (9·8%), then being the major product. It is possible that further variation of the reaction conditions will give an increased yield.

Structures of compounds (I and III—VII), are fully supported by their spectroscopic properties. The pure compounds (I, V, VI, and VII) gave satisfactory analytical data.

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[1] W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *Chem. Comm.*, 1969, 970.
[2] W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *Chem. Comm.*, 1969, 58.
[3] L. Crombie, personal communication.
[4] R. Stevens, *Chem. Rev.*, 1967, **67**, 43.
[5] T. Backhouse and A. Robertson, *J. Chem. Soc.*, 1939, 1257.