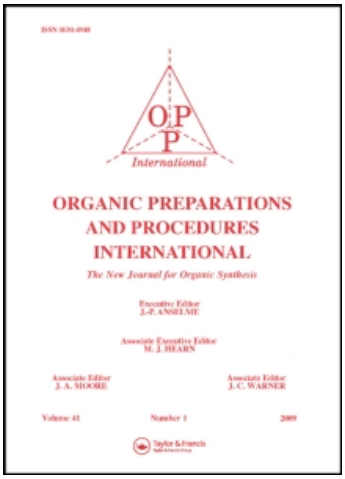

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A CONVENIENT SYNTHESIS OF 5,7-DIHYDROXYCHROMONE

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1H), 7.10-7.50 (8H), 9.80 (s, 1H, exchangeable).

Anal. Calcd. for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.12. Found: C, 67.88; H, 4.01

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A CONVENIENT SYNTHESIS OF 5,7-DIHYDROXYCHROMONE

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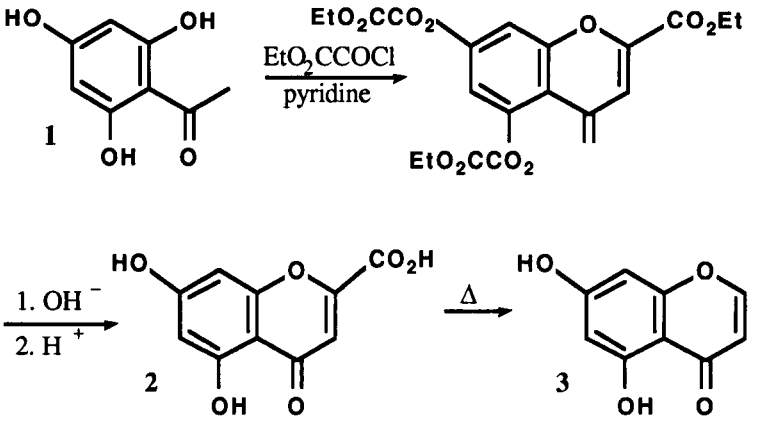
5,7-Dihydroxychromone (**3**) is a flavanoid decomposition product[1] that has been found as a constituent in certain plant extracts[2,3] and is a germination and growth inhibitor.[3] Purification of gram

quantities (needed for extensive growth regulatory experiments) is time consuming and published synthetic routes require the use of protecting groups and/or anhydrous conditions[4] that, when not rigorously maintained, give poor yields. The isoflavone synthesis described by Baker et al.[5] does not require such stringent attention and, as described here, will produce **3** even though the methyl group is not activated by a phenyl substituent, a condition previously thought to be necessary.[5] Other



substituted chromones can undoubtedly be prepared from the appropriate 2-hydroxyacetophenone.

EXPERIMENTAL SECTION[6]

5,7-Dihydroxychromone.- To a solution of 2,4,6-trihydroxyacetophenone monohydrate (2 g) in 25 ml of dry pyridine, cooled in an ice bath, 7.5 ml of ethyl oxalyl chloride was added dropwise with stirring. The mixture was allowed to come to room temperature and stirred overnight. The slurry was poured into water and extracted three times with $CHCl_3$. The combined $CHCl_3$ layers were washed with 10% HCl and the solvent was removed under reduced pressure. The residue was taken up in 50 ml of EtOH, 100 ml of 5% Na_2CO_3 was added and the mixture was stirred at 60-70° for 2 hrs. The ethanol was removed in vacuo, the solution acidified and the crude carboxylic acid (**2**) was collected (0.9 g). Heating small (100 mg) batches of the acid with a flame evolved 0.38 g (18%) of **3** collected as a pale yellow solid [mp. 267-269° (uncorr.), lit.[2] 272-273°], in an air-cooled condenser; it was chromatographically and spectroscopically identical to an authentic sample.[1-3] EIMS [70 eV m/e, (rel. int.)]: 178, (100, M^+), 150 (45), 124 (25), 96 (10), 69 (30). ^1H NMR (300 MHz, acetone-d_6): δ 12.7 (s, OH-5); 9.6 (s br, OH-7); 8.01 (d, J = 6, H-2); 6.35 (d, J = 2; H-8); 6.21 (d, J = 2, H-6); 6.16 (d, J = 6, H-3).

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6. Reactants and solvents were commercially available, reagent grade.

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AN IMPROVED PREPARATION OF A TRICYCLIC LACTONE, A POTENTIALLY USEFUL PRECURSOR OF HIGHLY FUNCTIONALIZED TERPENOIDS

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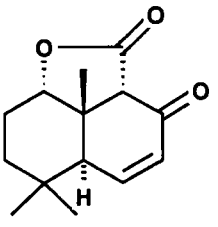
The tricyclic lactone **1** was found to be a valuable intermediate for the synthesis of the biologically important and highly oxygenated labdane diterpene forskolin **2**[1] and some 1-hydroxy-drimanes related to the sesquiterpene warburganal **3**.[2] The synthesis (and spectroscopic properties) of **1** *via* an intramolecular Michael addition (**4** → **5**) in tandem with an intramolecular aldol condensation (**5** → **1**), was reported almost simultaneously by Wu et al.[3] and by us.[4]



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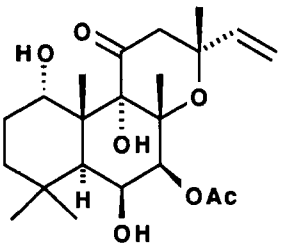

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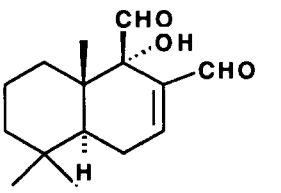

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