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SYNTHESIS OF TRIMETHYL ETHER OF FLEMIWALLICHIN - A.

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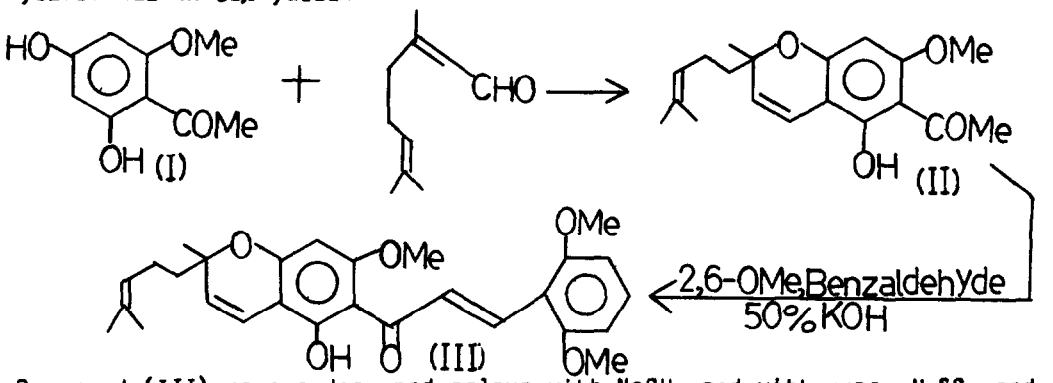
Recently Jagannadha Rao et al.[1] have reported the isolation of a new chromenochalkone, Flemiwallichin-A from the leaves of Flemingia Wallichin W & A.

We now wish to report the synthesis of the trimethyl ether of the above chalkone which has got a phloroglucinol nucleus. It has been found that the reaction between phloroacetophenone and citral gives products other than chromene. Hence the reaction between the 6-methyl ether of phloroacetophenone and citral was explored. The former was prepared from the trimethyl ether of phloroglucinol which with acetyl chloride gave the corresponding acetophenone. The latter on demethylation with aluminium chloride in chlorobenzene gave the 6-methyl ether (I) m.p. 200-201° (Reported[2] 203°).

Heating equimolar quantities of (I) and citral in pyridine at 145-50° for 10 hrs. gave on evaporation a gummy mass which was chromatographed on silica gel. Elution with benzene-pet.ether (40-60°) 3:2 gave in 60% yield a yellow solid crystallised from pet.ether (40-60°) m.p. 86-89°. The n.m.r. (CCl_4) showed bands at δ 1.35 (3H, s, OCH_3), 1.57 (3H, s); 1.67 (3H, s); 1.7 ∽ 2.25 (4H, m); 2.55 (3H, s, $CO-CH_3$); 3.85 (3H, s, OCH_3); 5.9 (1H, s,ar.); 13.4 (1H, s, chelated OH). The AB pattern of two doublets at 5.4 and 6.7 provides unambiguous evidence for the presence of the chromene ring[3]. i.r. (CH_2Cl_2) ν_{max} 3000-3250 cm^{-1} broad OH, >C=O band at 1620 cm^{-1} is an indication of a strongly chelated -OH with an adjacent carbonyl group. Mass spectrum reveals the molecular weight of 316 corresponding to chromeno-acetophenone (II), while other peaks were obtained at m/e 301 (M-15) and

m/e 233 (M-83). This fragmentation pattern is in full agreement with that reported by Merlini et al.[4] for a chromene structure. The ketone (II) on an aldol condensation with 2,6-dimethoxy-benzaldehyde in the presence of alcoholic potassium hydroxide (50%) under N_2 and after usual workup gave a sticky mass which on chromatography over silica gel with hexane-AcOEt 85:15 afforded the trimethyl-ether of flemiwallichin-A (III) as a thick yellow oil in 60% yield.



Compound (III) gave a deep red colour with NaOH, red with conc. H_2SO_4 and a characteristic test for chalkones with $SbCl_3$ in CCl_4, yielding a red precipitate. N.M.R. of (III) (CCl_4) showed the absence of CO $\underline{CH_3}$ group and appearance of chalkone peaks at δ 8.15 and 8.4 in addition to the usual peaks. Mass spectrum confirms the molecular weight as 464 and also showed two principal peaks at m/e 449 (M-15), and at 381 (M-83).

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