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TOTAL SYNTHESIS OF EROSNIN

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Erosnin was isolated from the seeds of Pachyrrhizus erosus (Yam beans), and its chemical structure (I) was established by Eisenbeiss and Schmid in 1959 (1). In this paper, we wish to report the total synthesis of this compound.

The synthesis of a key intermediate (II) was accomplished by the following two routes. 5-Hydroxy-6-acetylbenzofuran (III) was prepared from methyl 6-benzyloxybenzofuran-2-carboxylate (2) through the modified synthetic way (3). The o-hydroxydeoxybenzoin moiety was easily condensed with ethyl carbonate in the presence of sodium to form hydroxycoumarin (4), thus from III was obtained 5-hydroxypsoralene (II), m.p. 251-252°C (IR 1692 cm^{-1}(α-pyrone)(Nujol), UV λ_{max}^{EtOH} $m\mu$(log ε) 222(4.35) 288(3.94) 325(4.12)). On the other hand, the dehydrogenation of 5-methoxy-2,3-dihydropsoralene which obtained from 5-hydroxy-6-acetyl-2,3-dihydrobenzofuran (5), was carried out with N-bromosuccinimide giving 5-methoxypsoralene (IV), m.p. 217-218°C (IR 1728 cm^{-1} (α-pyrone) (Nujol), UV λ_{max}^{EtOH} mμ (log ε) 237(4.43) 287(4.03) 321(3.97) (lit. (6) m.p. 216-217°C)). The ether cleavage reaction of IV with hydrobromic acid gave the above compound (II).

The dehydrogenatic condensation of II and catechol in the presence of potassium ferricyanide by the method of Wanzlick et al. (7) gave furano(3',2':6,7)-5",6"-dihydroxybenzofurano(3",2":3,4)coumarin (V), m.p.>300°C, which on methylation afforded the corresponding dimethyl ether (VI), m.p. 286-287°C (IR 1738 cm^{-1} (α-pyrone) (KBr), UV λ_{max}^{EtOH} mμ (log ε) 239(4.60) 280(3.98) 355(4.35), Found: C, 67.73, H, 3.71. Calcd. for $C_{19}H_{12}O_6$: C, 67.85, H, 3.60). Finally, according to the previous reported method (8), the methylenation with methylene iodide, V yielded erosnin (I), m.p.>330°C (IR 1735, 1636, 1578, 1506, 1265, 938 cm^{-1} (KBr), UV λ_{max}^{EtOH} mμ (log ε) 239(4.58) 285(3.95) 354(4.30) 366(4.26), Found: C, 67.22, H, 2.63. Calcd. for $C_{18}H_8O_6$: C, 67.50, H, 2.52)(lit. (1) m.p. ca. 350°C, IR 1733, 1639, 1582, 1506, 1266, 937 cm^{-1} (KBr)). The infrared and ultraviolet spectra were superimposable on that of natural erosnin.

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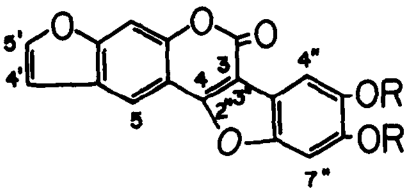

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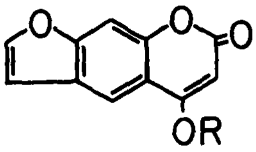
V R = H
VI R = CH_3



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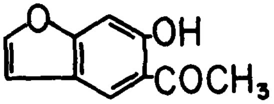
IV R = CH_3



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