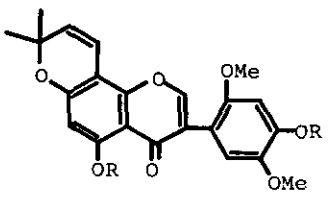
SYNTHESES OF PYRANOISOFLAVONES FROM THE CORRESPONDING CHALCONES WITH THALLIUM(III) NITRATE

M. Tsukayama, Y. Iguchi, T. Horie, M. Masumura, and M. Nakayama*
Department of Applied Chemistry, Faculty of Engineering, Tokushima University, Tokushima 770, Japan. *Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan.

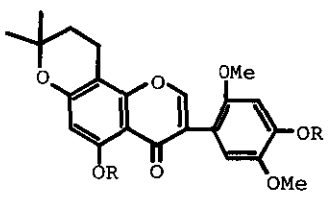
Elongatin was isolated from the roots and aerial parts of *Tephrosia elongata* E. Mey. and the structure has been assigned to be a linear pyranoisoflavone (4',5-dihydroxy-2',5'-dimethoxy-2",2"-dimethylpyrano[5",6"-g]isoflavone (1) on the basis of chemical and spectroscopic evidence.[1] We report here syntheses of (1) and an angular pyranoisoflavone (toxicarol isoflavone methyl ether) (2).

The partial benzylation of 5,7-(dihydroxy)chroman (4) with benzyl chloride gave 7-(benzyloxy)chroman (5) (mp 113-115 °C). The condensation of (5) with 4-benzyloxy-2,5-dimethoxybenzaldehyde (3) gave the corresponding chalcone (6). The oxidative rearrangement of the acetate (7) of (6) with thallium(III) nitrate (TTN) in methanol, followed by the hydrolysis with diluted hydrochloric acid gave angular isoflavone (8), which was converted into 4',5-(dihydroxy)isoflavone (9) (mp 205-206 °C) by the hydrogenolysis with Pd-C. The dehydrogenation of (9) with DDQ gave the isomer (10) (mp 171-173 °C) of elongatin (1). Compound (10) was converted into (2) (mp 179-180 °C).

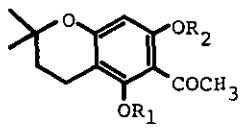
The hydrolysis of 7-(tosyloxy)chroman (11), which was synthesized from (4), gave 5-(benzyloxy)chroman (12) (mp 99-100 °C). The chroman (12) was condensed with (3) to give chalcone (13). According to the method described above, the acetate (14) of (13) was treated with TTN and acid to give linear isoflavone (15), which was debenzylated to dihydroelongatin (16) (mp 181-183 °C). The dehydrogenation of (16) with DDQ gave the desired pyranoisoflavone (1) (mp 178-179 °C). Compound (1) was converted into the diacetate (17) (mp 227-228 °C).



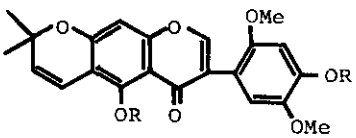
(2) R=Me
(10) R=H



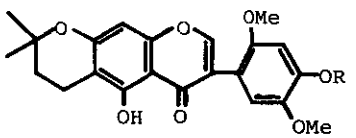
(8) R=$C_6H_5CH_2$
(9) R=H



(4) R_1=R_2=H
(5) R_1=H, R_2=$C_6H_5CH_2$
(11) R_1=$C_6H_5CH_2$, R_2=Ts
(12) R_1=$C_6H_5CH_2$, R_2=H



(1) R=H
(17) R=CH_3CO



(15) R=$C_6H_5CH_2$
(16) R=H

1) T.M.Smalberger, R.Vleggaar, and J.C.Weber, Tetrahedron, 31, 2297(1975).