Synthesis of Tachrosin, a Natural Flavone Substituted by a Novel Furanoid Ring System

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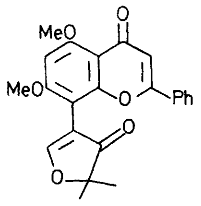
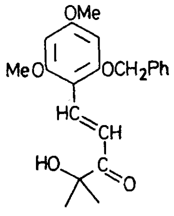
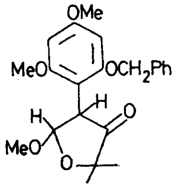
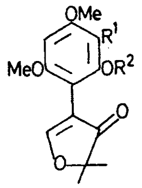
Summary Tachrosin, 5,7-dimethoxy-8-(2,3-dihydro-2,2-dimethyl-3-oxofuran-4-yl)flavone (**1**), was synthesised using the oxidative rearrangement of a 5-aryl-2-hydroxypent-4-en-3-one (**2**) with $Tl(NO_3)_3$ in methanol to a 4-aryl-5-methoxytetrahydrofuran-3-one (**3**) followed by elimination of the elements of methanol to form the dihydrofuranone ring.


(1)


(2)


(3)


(4) $R^1 = H$, $R^2 = CH_2Ph$
(5) $R^1 = R^2 = H$
(6) $R^1 = COMe$, $R^2 = H$
(7) $R^1 = COMe$, $R^2 = COPh$
(8) $R^1 = COCH_2COPh$, $R^2 = H$

Tachrosin (**1**), a novel type of natural flavone, has recently been isolated from *Tephrosia polystachyoides*[1] and contains an isoprenoid side chain incorporated into the unprecedented 4-aryl-2,3-dihydrofuran-3-one ring system. The first total synthesis of (**1**) was accomplished by the following sequence of reactions.

Condensation of 2-benzyloxy-4,6-dimethoxybenzaldehyde, m.p. 98—100 °C, with 3-hydroxy-3-methylbutan-2-one gave (**2**), m.p. 131—133 °C, which when treated with $Tl(NO_3)_3$ in methanol gave by oxidative rearrangement[2,3] a mixture of the epimers of (**3**). Methanol was eliminated by treatment with acid to afford the dihydrofuranone (**4**), m.p. 107—109 °C. Debenzylation to (**5**), m.p. 85—87 °C, Hoesch-acetylation to (**6**), m.p. 148—150 °C, benzoylation to (**7**), m.p. 144—145 °C, base-catalysed benzoyl migration to the dibenzoylmethane (**8**), m.p. 171—172 °C, and finally cyclisation by dehydration gave tachrosin. The overall yield from the benzaldehyde was 8·2%. All intermediates were characterised by elemental analysis, and ^1H n.m.r. and i.r. spectra. The spectral data for (**1**), including mass spectra were identical with those reported for natural tachrosin.[1]

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[1] T. M. Smalberger, R. Vleggaar, and H. L. de Waal, *J. S. African Chem. Inst.*, 1971, **24**, 1.
[2] A. McKillop, B. P. Swann, M. E. Ford, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3641.
[3] L. Farkas, A. Gottsegen, M. Nógrádi, and S. Antus, *J.C.S. Perkin I*, 1974, 305.