

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

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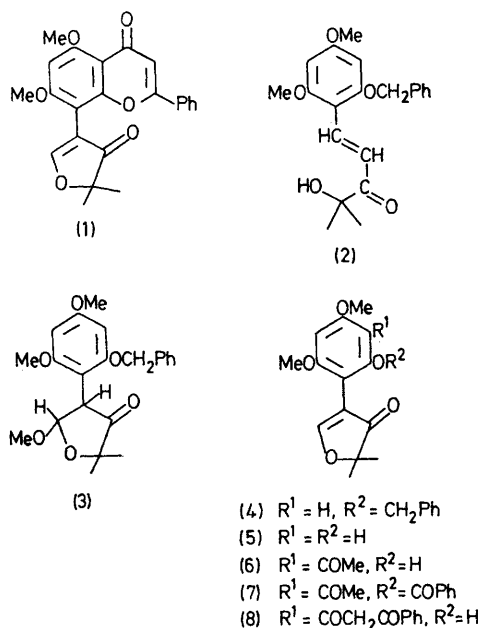
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**Summary** Tachrosin, 5,7-dimethoxy-8-(2,3-dihydro-2,2-dimethyl-3-oxofuran-4-yl)flavone (**1**), was synthesised using the oxidative rearrangement of a 5-aryl-2-hydroxypent-4-en-3-one (**2**) with  $\text{Ti}(\text{NO}_3)_3$  in methanol to a 4-aryl-5-methoxytetrahydrofuran-3-one (**3**) followed by elimination of the elements of methanol to form the dihydrofuranone ring.

TACHROSIN (**1**), a novel type of natural flavone, has recently been isolated from *Tephrosia polystachyoides*<sup>1</sup> 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  $\text{Ti}(\text{NO}_3)_3$  in methanol gave by oxidative rearrangement<sup>2,3</sup> 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 <sup>1</sup>H n.m.r. and i.r. spectra. The spectral data for (**1**),



including mass spectra were identical with those reported for natural tachrosin.<sup>1</sup>

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<sup>2</sup> A. McKillop, B. P. Swann, M. E. Ford, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3641.

<sup>3</sup> L. Farkas, A. Gottsegen, M. Nógrádi, and S. Antus, *J.C.S. Perkin I*, 1974, 305.