Synthesis of Pulvinones, Metabolites of *Aspergillus terreus* and *Suillus grevillei*

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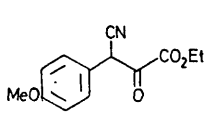
Summary A total synthesis of 2-phenyl-4-benzylidenetetronic acids ('pulvinones') (**7**), pigments found in *Aspergillus terreus* and *Suillus grevillei*, is described.

'PULVINONE' is the generic name applied to a group of substituted 2-phenyl-4-benzylidenetetronic acid pigments isolated recently from the larch mushroom *Suillus grevillei*[1] and from cultures of *Aspergillus terreus*.[2] Although pulvinones have been obtained from thermal rearrangement of 2,5-diarylcyclopentane-1,3,4-triones[3] and from degradation of fungal and lichen pulvinic acids,[4] hitherto no unambiguous synthesis of unsymmetrically substituted pulvinones has been reported. We now describe a total synthesis of these pigments.

Condensation between *p*-methoxyphenylacetonitrile and diethyl oxalate led first to (**1**) which with Me_2SO_4 gave (90%) the cinnamate (**2**). Hydrolysis of (**2**) with H_2SO_4–HOAc then produced the substituted maleic anhydride (**3**).[5] Reduction of (**3**) with $Li(OBu^t)_3AlH$ or $LiAlH_4$ was completely regiospecific and gave (*ca.* 80%) a 2:1 mixture of the lactol (**5**) and the lactone (**4**), needles, m.p. 111—112 °C, ν_{max} 1726 and 1637 cm^{-1}, τ 2·11 (2H, d, *J* 9 Hz), 3·08 (2H, d, *J* 9 Hz), 5·0 (CH_2), 5·94 (OMe), and 6·23 (OMe), which were separated by chromatography. Reduction of (**5**) with $NaBH_4$ in aq. NaOH also gave (**4**).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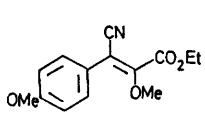
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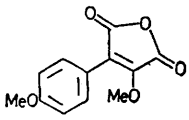
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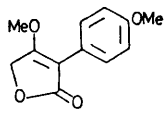
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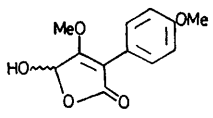
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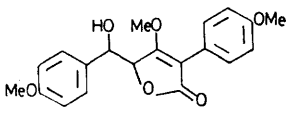
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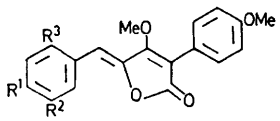
(7) a; R^1 =OMe, R^2 = R^3 =H
b; R^1 = R^2 =OMe, R^3 =H
c; R^1 = R^3 =OMe, R^2 =H

Reaction of the lactone (**4**) with lithium *N*-cyclohexyl-*N*-isopropylamide at −70 °C produced the corresponding anion which with *p*-anisaldehyde gave (90%) the carbinol (**6**). Dehydration of (**6**) in hot benzene with *p*-$MeC_6H_4SO_3H$ followed by chromatography and crystallisation gave *O*-methyl-4,4′-dimethoxypulvinone (**7a**), golden needles, m.p. 137—138·5 °C, identical (mixed m.p., t.l.c., and spectral data) with a natural sample from *A. terreus*.[2] In a similar manner, the lactone (**4**) with 3,4-dimethoxybenzaldehyde gave the pulvinone (**7b**), yellow-green plates, m.p. 153—154 °C, identical with that obtained from *S. grevillei*.[1] The isomeric *O*-methyl-2′,4′,4-trimethoxypulvinone (**7c**), m.p. 167—167·5 °C, λ_{max} 373·5 nm, ν_{max} 1750 and 1626 cm^{-1}, τ 1·9 (1H, d, *J* 9 Hz), 2·57 (2H, d, *J* 9 Hz), 3·13 (2H, d, *J* 9 Hz), 3·32 (1H), 3·51 (1H, dd, *J* 2 and 9 Hz), 3·6 (1H), and 6·19—6·22 (4 × OMe), was also synthesised; this pulvinone was not identical (m.p. and spectral data) with a pulvinone purported to have this constitution and isolated from *A. terreus*.[2]

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[2] N. Ojima, S. Takenaka, and S. Seto, *Phytochemistry*, 1975, **14**, 573.
[3] L. Claisen and T. Ewan, *Annalen*, 1895, **284**, 245.
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[5] *Cf.* R. L. Edwards and M. Gill, *J.C.S. Perkin I*, 1973, 1538.