Tetrahedron Letters,Vol.29,No.17,pp 2085-2088,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

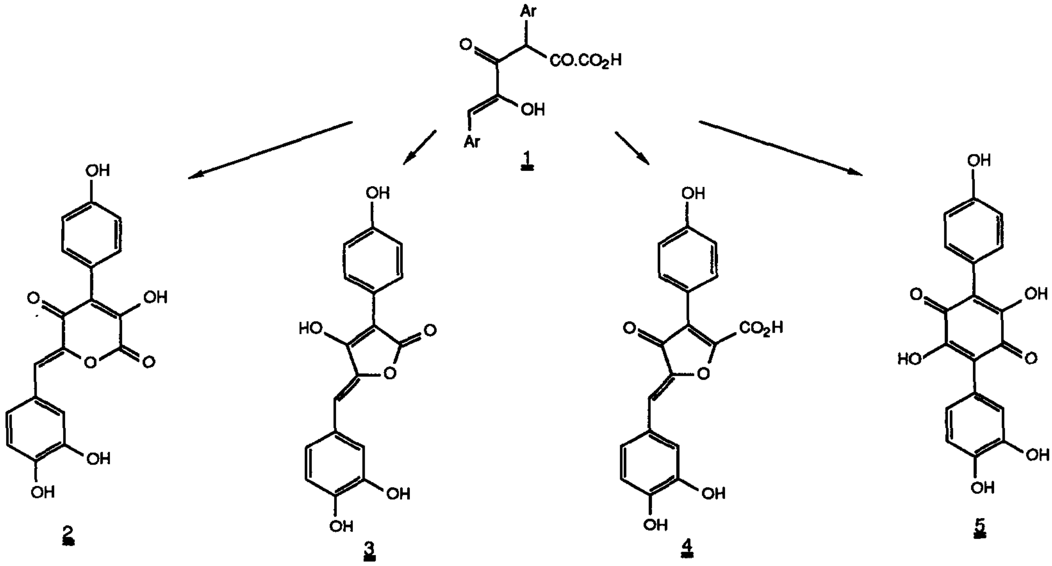
SYNTHESIS OF FUNGUS PIGMENTS OF THE GREVILLIN AND PULVINONE TYPES FROM BENZYLACYLOINS.[1]

Melvyn Gill* and Milton J. Kiefel

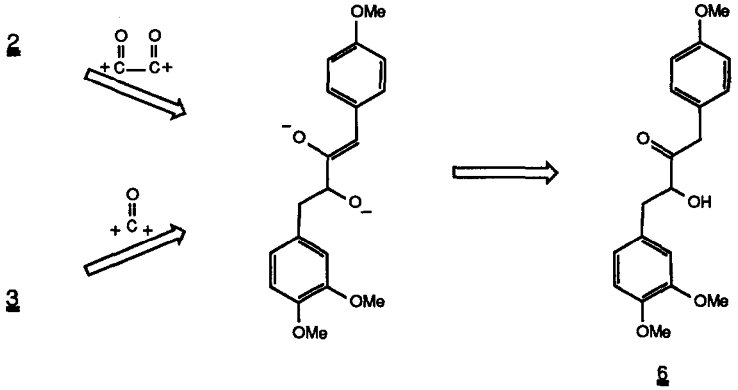
Department of Organic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia.

Summary - Grevillin-B (2) and 3',4',4-trihydroxypulvinone (3), principal colouring matters of the mycorrhizal toadstool *Suillus grevillei*, are synthesised in good yield from a common precursor in the form of the benzylacyloin 6.

Many fungi have developed pathways by way of which aromatic amino acids are converted to pigments.[2] Mushrooms and toadstools belonging to the order Boletales appear to be particularly adept in this capacity and a broad spectrum of colouring matters have been isolated from the fruit bodies of these fungi.[3] With the expansion and development of the chemistry of the group it has become clear that many of these pigments, e.g., the grevillins, pulvinones, furanones and terphenylquinones exemplified by formulae 2-5, respectively, could arise *in vivo* from a common progenitor of the type 1 (Scheme 1).[2,3] We recognised some time ago[4] that these pigments should all be available synthetically both directly, as detailed in part below, and *via* the putative bio-intermediate 1, from the benzylacyloin 6. Importantly, in this approach the nature of the acyloin effectively controls the relative disposition of the aromatic residues as is required in the natural products 2, 3 and 4.[5] Accordingly, we recently developed a versatile and unambiguous approach to unsymmetrically disposed benzylacyloins including 6.[6]



Scheme 1

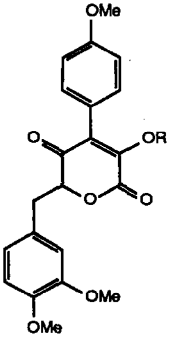


Scheme 2

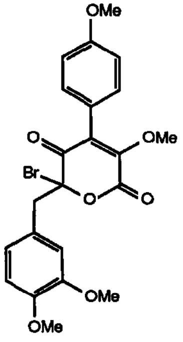
We report here the synthesis of fungus pigments of the grevillin[7] and pulvinone types in which we successfully apply the concept outlined in retrosynthetic terms in Scheme 2 beginning from the benzylacyloin 6.

Double deprotonation of 6 [LDA (2.3 equiv.), THF, -78°] followed by addition of oxalyldi-imidazole (2.4 equiv., -78°→0°) gave the dihydrogrevillin 7 (56%).[8] Exposure of 7 to an excess of ethereal diazomethane gave 8 (93%) which, despite numerous attempts, resisted direct dehydrogenation. However, bromination of 8 (NBS, hν, CCl_4 reflux, 5 min.) followed immediately by treatment of the bromo derivative 9 with Hünig's base (CCl_4, amb. temp., 10 min.) afforded the tetramethyl derivative 10 of grevillin-B (2) in 80% yield from 8. Demethylation of 10 (BBr_3, CH_2Cl_2 reflux, 3h) gave the red grevillin-B (2) which was spectroscopically and chromatographically indistinguishable from that pigment isolated from the toadstool *Suillus grevillei*.[9,10,11]

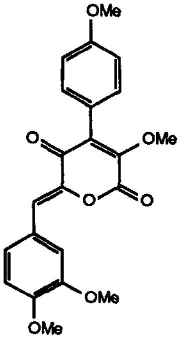
Since methods are already in place for the transformation of grevillins, including 10, into terphenylquinones[12] and these, in turn, into pulvinic acids,[13] our approach may be viewed also as an entry into these two further major groups of fungus pigments.



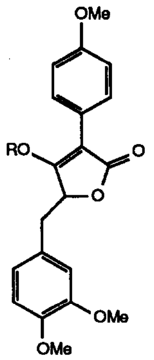
7 R=H
8 R=Me



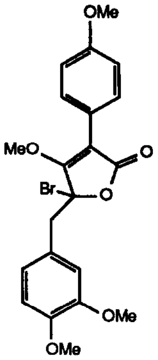
9



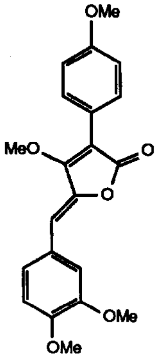
10



11 R=H
12 R=Me



13



14

For pulvinone synthesis the enolate-alcoholate derived from 6 (as above) was intercepted with carbonyldi-imidazole (2.4 equiv., -78°→0°).[14] The dihydropulvinone 11 (50%) so obtained was methylated (dimethyl sulphate, K_2CO_3, acetone) to give 12 (80%).[15] Bromination of 12 (NBS, hν, CCl_4 reflux, 5 min.) gave 13 (75%) which was smoothly dehydrobrominated (DBU, benzene, 30 min.) to afford 3',4',4-trimethoxy-O-methylpulvinone (14) (85%) identical in all respects with the permethyl derivative of the natural product 3.[9]

Acknowledgement - We thank Professor G. Pattenden, University of Nottingham, for a copy of his paper cited in ref. 7 prior to publication, and the Australian Research Grants Scheme for continuing financial support. M.J.K. is grateful for a Commonwealth Postgraduate Research Award.

References and Footnotes

1. Pigments of Fungi, Part 9. For Part 8 see: M. Gill, A. Giménez and R. W. McKenzie, Aust. J. Chem., in press.
2. For a comprehensive review: M. Gill and W. Steglich, Fortsch.der Chem. org. Naturstoffe, 1987, 51, 1.
3. M. Gill and R. Watling, Plant Syst. and Evol., 1986, 151, 225.
4. M. Gill and D. A. Lally, Royal Australian Chemical Institute 8th National Conference, University of Western Australia, Perth, W.A., May 13-18, 1984, Abstracts p. 35.
5. For other syntheses of pulvinones and pulvinic acids in which this problem is addressed see, *inter alia*: R. L. Edwards and M. Gill, J. Chem. Soc. Perkin Trans. I, 1973, 1921; R. L. Edwards and M. Gill, J. Chem. Soc. Perkin Trans. I, 1973, 1529; D. W. Knight and G. Pattenden, J. Chem. Soc. Perkin Trans. I, 1979, 70; D. W. Knight and G. Pattenden, J. Chem. Soc. Perkin Trans. I, 1979, 84; R. Ramage, G. J. Griffiths, F. E. Shutt and J. N. A. Sweeney, J. Chem. Soc. Perkin Trans. I, 1984, 1593; R. Ramage, G. J. Griffiths and J. N. A. Sweeney, J. Chem. Soc. Perkin Trans. I, 1984, 1547.