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STRUCTURAL REVISION FOR PRENYLATED PULVINONE METABOLITES FROM ASPERGILLUS TERREUS

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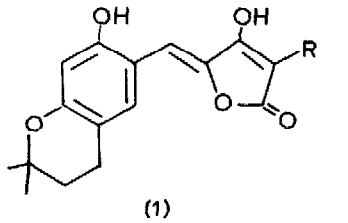
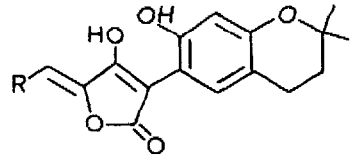
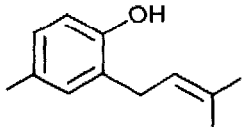
On the basis of extensive degradation and spectroscopic studies, structures (1a-c) were earlier assigned to three prenylated pulvinone pigments from Aspergillus terreus.[1] The incidence of thermal equilibration amongst pulvinones[2] via diarylcyclopentan-2,3,5-triones (viz 3), and our contemporaneous synthetic studies,[3] led us to question the structures (1a-c). Accordingly we have now re-examined the structures of these metabolites by single crystal X-ray analysis and comparative spectral data.

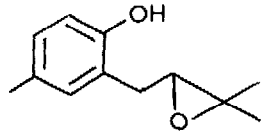


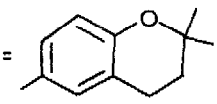
(1)

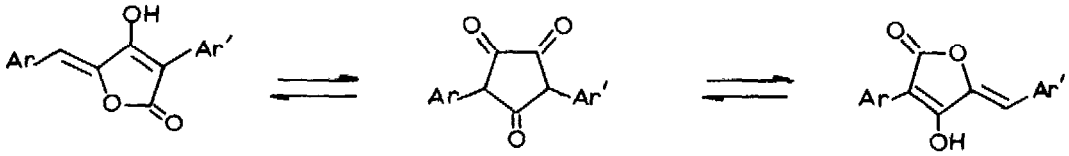


(2)

a R= 

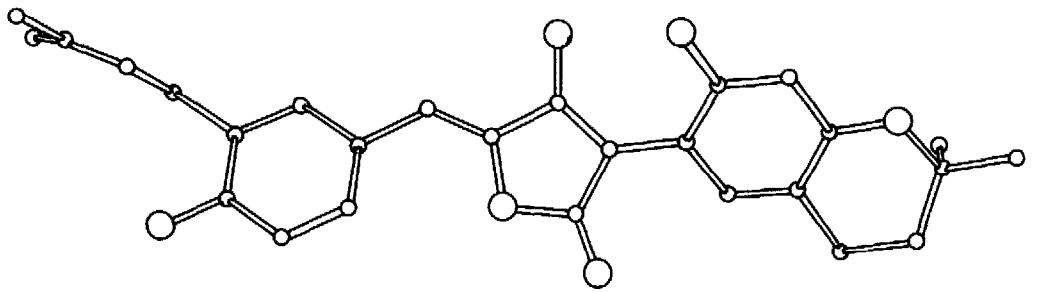
b R= 

c R= 



(3)

The prenylated pulvinone from A. terreus assigned constitution (1a), $C_{27}H_{28}O_6.1.5\ H_2O$, m.p. 257-258°, crystallised from methanol in the triclinic space group $P\bar{1}$ with a=9.55, b=11.02, c=13.44Å, α=102.94, β=113.73, and γ=91.39° and Z=2. Intensity data were collected on an automatic four-circle diffractometer using Mo-K_α radiation and a total of 2144 reflections were considered observed. The structure was solved by direct methods using the Multan programme,[4] and has so far been refined by block-diagonal least squares to a



FIGURE

current R-index of 6.9%. The structure of the pulvinone thus revealed is shown in the Figure. One molecule of water is hydrogen-bonded to a molecule of the pulvinone and the other water molecule is disordered and approximately sited on a crystallographic centre of symmetry forming no hydrogen bonds.

The pulvinone metabolites (1a-c) exhibit several features in common in their p.m.r. spectra, and strong similarities are clear in their m.s. fragmentation patterns. These and other data support a similar 2-(hydroxy-2,2-dimethylchroman)tetronic acid formulation (viz 2) for all three metabolites.

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References

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4. G. Germain, P. Main and M.M. Woolfson, Acta Cryst., A27, 368 (1971).