

SPECIALIA

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Two Novel Metabolites of *Aspergillus fonsecaeus*

A previous investigation into the metabolic products of *Aspergillus fonsecaeus* (N.R.R.L. 67, 16-1)¹ led to the isolation of the yellow substance fonsecin, the structure of which was subsequently established as I².

This report deals with 2 minor pigments which we have isolated from the same source, having the structures II and IV. They possess a naphthopyranone nucleus like the known pigments fonsecin (I)² and rubrofusarin (III)³, from which they turn out to be the corresponding naturally occurring monomethyl ethers. We propose for them the names fonsecin B and rubrofusarin B, respectively.

The mixture of pigments was extracted with ethyl acetate from the air-dried mycelium. Dried extracts afforded a solid residue (3 g) which was submitted to chromatography on a silicic acid column. The methylene chloride eluates contained a yellow band from which crystallized rubrofusarin B (IV), (65mg), yellow needles, m.p. 213° (chloroform-benzene). The NMR-spectrum (DMSO-d₆) showed the following signals: δ 2.36 ppm (3H, s, CCH₃); 3.88 (6H, s, 2 OCH₃); 6.12 (1 H, s, C₃-H); 6.43 (1 H, d, J = 2.5 Hz, C₇-H); 6.78 (1 H, d, J = 2.5 Hz, C₉-H); 7.09 (1 H, s, C₁₀-H); 14.77 (1H, s, OH) indicating that rubrofusarin B can be formulated as 2-methyl-5-hydroxy-6,8-dimethoxy-4H-naphtho [2,3-b] pyran-4-one (IV) further confirmed by a mixed fusion, comparison of IR-spectra and thin layer chromatography (silica gel, chloroform, R_f 0.40) with an authentic sample. This

compound is a natural *o*-methyl derivative of rubrofusarin and was previously prepared by methylation of natural rubrofusarin and chemical synthesis by SHIBATA et al.⁴, who named it rubrofusarin monomethylether B.

The second compound of the above-mentioned column was eluted by increasing the polarity of the solvent and, after further purification by TLC, crystalline fonsecin B (II) was obtained (68 mg), yellow needles, m.p. 176° (acetone-water). Fonsecin B proved to be identical with the monomethylether of fonsecin, prepared by treating the latter with diazomethane², by IR, mixed m.p. and TLC (silica gel, chloroform:methanol 97:3, R_f 0.67) and its structure is therefore 2-methyl-2,5-dihydroxy-6,8-dimethoxy-2,3-dihydro-4H-naphtho [2,3-b] pyran-4-one (II). The NMR-spectrum (DMSO-d₆) of fonsecin B exhibited the following signals: δ 1.62 ppm (3H, s, CCH₃); 2.83 (1H, s, C₃-H); 3.07 (1H, s, C₃-H'); 3.85 (6H, s, OCH₃); 6.37 (1H, d, J = 2.5 Hz, C₇-H); 6.56 (1H, s, C₁₀-H); 6.69 (1H, d, J = 2.5 Hz, C₉-H); 7.01 (1H, broad s, C₂-OH); 14.10 (1H, s, C₅-OH) which are in agreement with structure (II).

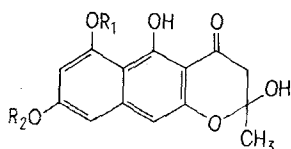
We also report here that rubrofusarin B can be obtained by chemical dehydration of fonsecin B, applying the conditions stated by TRAYNELIS et al.⁵ for the dehydration of alcohols. When fonsecin B (10 mg) in dimethylsulfoxide (1 ml) was heated for 8 h at 170°C dehydration occurred and a crystalline dehydrated product could be obtained by removal of the solvent and TLC. It was shown to be identical with rubrofusarin B by IR, mixed m.p. and TLC. This dehydration is another example of the similar reaction described for 2-hydroxychromanone compounds⁶.

The proposed hydroxypyranone structures for fonsecin (I) and fonsecin B (II) and the close structural relation of these substances with rubrofusarin (III) are confirmed⁷.

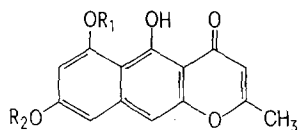
Resumen. Del *Aspergillus fonsecaeus* (N.R.R.L. 67, O 16-1) se han aislado dos nuevos pigmentos que fueron identificados como monometil éteres de la fonsecina y de la rubrofusarina, respectivamente.

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I: R₁ = CH₃, R₂ = H
II: R₁ = R₂ = CH₃



III: R₁ = H, R₂ = CH₃
IV: R₁ = R₂ = CH₃

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⁵ V. J. TRAYNELIS, W. L. HERGENROTHER, J. R. LIVINGSTON and J. A. VALICENTI, J. org. Chem. 27, 2377 (1962).

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