New Metabolites of *Aspergillus amstelodami* Related to the Biogenesis of Neoechinulin

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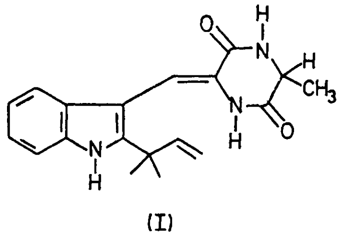
Summary The mycelium of *Aspergillus amstelodami* has been found to contain three new prenylated indole metabolites, neoechinulin A (I), neoechinulin B (II), and neoechinulin C (III), which are relevant for the biogenesis of neoechinulin (IV).

IN the course of a study on the time-dependent elaboration of metabolites involved in echinulin[1]–neoechinulin[2] biosynthesis in sugar beet molasses cultures of *Aspergillus amstelodami*, three new prenyl indole derivatives were isolated from the ether extracts of the mycelium and characterised: neoechinulin A (I), B (II), and C (III). We report here on their structures.

The structures of neoechinulin A (I), ivory crystals m.p.

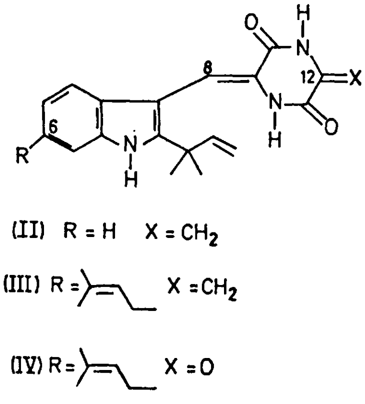
264—265°, B (II), yellow crystals, m.p. 234—236°, and C (III)† yellow crystals, m.p. 205—207°, were confirmed by their u.v., n.m.r. and mass spectra. The essential differences in the n.m.r. spectra between (I) and (II) consisted of the absence of a –CH*Me* doublet at δ 1·42 and the appearance of $:CH_2$ at δ4·78, 5·09 for (II), and between (II) and (III) the main difference consisted of the additional resonances for the $Me_2C{=}CCH_2$– group for (III). Structures (I)—(III) were further confirmed by comparison with echinulin[1] and neoechinulin.[2] Conclusive evidence for structure (III) was provided by chemical degradation. Alkaline hydrolysis of (III) afforded 2-α,α-dimethylallyl-6-γ,γ-dimethylallylindole and the corresponding 3-formylindole as already observed in the hydrolysis of neoechinulin.[2]



(I)

The structures of neoechinulin A,B, and C (I—III) are particularly interesting in view of a possible biogenetic relationship with neoechinulin (IV): (I) → (II) → (III) → (IV), outlining a completely new oxidation mechanism (CH-Me → C=O *via* a C=CH$_2$ group). The incorporation (1·2%) of *cyclo*-L-alanyl-L-tryptophyl (methylene-C^{14}) in neoechinulin seems to corroborate such a hypothesis.

Furthermore, the isolation of (I) adds more evidence to that proposed by Allen[3] for echinulin, i.e. that the first isopentenyl chain is introduced at the 2-position of a preformed *cyclo*-alanyltryptophyl system.



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† While this paper was being prepared, we were informed by Profs. C. Fuganti and D. Ghiringhelli of their discovery of this compound

[1] A. Quilico, *Res. Progr. Org. Biol. Medicin. Chem.*, 1964, **1**, 1964.

[2] G. Casnati, A. Pochini, and R. Ungaro, *Gazzetta*, 1973, **103**, 141.

[3] C. M. Allen, Jr., *Biochemistry*, 1972, **11**, 2154.