

SPECIALIA

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Neoechinulin D, a New Isoprenylated Dehydrotryptophyl Metabolite from *Aspergillus amstelodami*

Moulds of the genus *Aspergillus* were previously shown to contain a number of closely related isoprenylated dehydrotryptophyl derivatives containing a dioxo or trioxopiperazine ring, all of which are characterized by an α , α -dimethylallyl chain at the 2-position of the indole nucleus¹⁻⁴.

We report here isolation and structural determination of a novel isoprenylated dehydrotryptophyl metabolite from *Aspergillus amstelodami*, which we called neoechinulin D.

Physical and chemical data clearly indicated that the new compound is cyclo-alanyl-2- α , α -dimethylallyl-6- γ , γ -dimethylallyl dehydrotryptophyl (I): m/e 391 M⁺ [C₂₄H₂₉N₃O₂]; λ_{max}^{EtOH} (log ϵ) 231 (4.53), 265 sh (4.06), 296 (4.02), 345 (4.04)⁵ nm; ν_{max} (KBr) 3340, 2940, 1670, and 1630 cm⁻¹. In the ¹H NMR-spectrum (CDCl₃) a signal at δ 7.10 accounted for the proton present on the double bond, conjugated to the aromatic system (C₈-H), consistently with that of neoechinulin¹, while the presence of the cyclo-alanyl moiety was confirmed by two signals at δ 4.20 (quartet of doublets), and at 1.56 (d) [J_{H-NH} 6 Hz, J_{H-CH₃} 1 Hz].

The structure was further confirmed by comparison with the corresponding data of echinulin⁶, neoechinulin¹ (II), and neoechinulin A (III), B (IV), and C (V)².

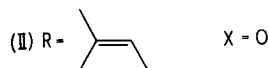
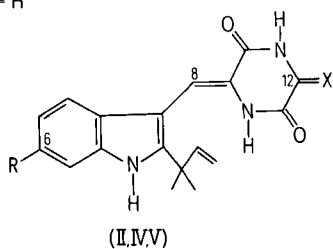
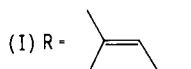
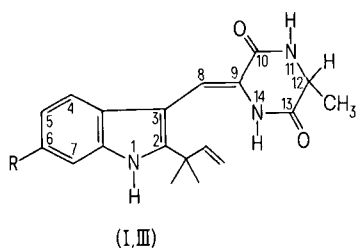
On alkaline hydrolysis (with 0.1 N NaOH/EtOH at 75°C for 24 h) neoechinulin D afforded 2- α , α -dimethylallyl-6- γ , γ -dimethylallyl indole and the corresponding 3-formylindole, identified by comparison with the products obtained from the hydrolysis of neoechinulin and neoechinulin C. All the chemical and the spectrographical data were consistent.

Catalytic (Pt from PtO₂) hydrogenation of neoechinulin D at 120 atm., room temperature, afforded a compound whose data were consistent with the hydrogenated neoechinulin C: m/e 395 M⁺ [C₂₄H₃₃N₃O₂]. In the ¹H NMR (CDCl₃), both the allylic chains appear hydrogenated while the unsaturation C₈-C₉ remains at δ 7.10 (1 H, s).

Summary. Isolation and structural determination of a novel isoprenylated dehydrotryptophyl metabolite from *Aspergillus amstelodami*, neoechinulin D, is reported.

A. DOSSENA, R. MARCHELLI and A. POCHINI

Istituto Policattedra di Chimica Organica dell'Università, Via Massimo d'Azeglio 85, I-43100 Parma (Italy), 23 June 1975.



Neoechinulin D was isolated from the crude ethereal extract of the mycelium (74 g) by column chromatography over silica gel 60 (Merck 70–230 mesh) eluted with hexane: ethyl acetate (1:1); 100 ml fractions were collected. After check TLC, the fractions 54–83 combined gave a compound (100 mg) which was further purified by preparative TLC and crystallized from petroleum ether: benzene as ivory crystals m.p. 223–225°C; $[\alpha]_D^{20} = -1.3$.

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