ISOLATION OF GLIOVICTIN FROM THE MARINE DEUTEROMYCETE ASTEROMYCES CRUCIATUS

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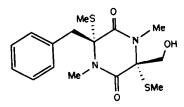
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Key Word Index—Asteromyces cruciatus; Deuteromycetes; Hypomycetales; marine fungus; gliovictin; diketopiperazines.

Abstract—(-)Gliovictin, a diketopiperazine isolated from terrestrial fungi of the genera Helminthosporium and Penicillium, has been isolated from culture broths of the marine deuteromycete Astermyces cruciatus.

The paucity of chemical information defining the metabolic products of marine fungi [1] prompts us to report upon our investigation of the marine deuteromycete Asteromyces cruciatus F. et Moreau ex Hennebert. This obligate marine fungus is frequently isolated from drift wood and from both living and decaying marine algae [2]. An isolate of A. cruciatus, F156, was first subcultured on seawater agar plates and the mycelia were transferred to liquid media [3, 4] and further cultivated at 25° for 21 days. The mycelia and culture media were separated by filtration and extracted individually with ethyl acetate. Mycelia yielded only triglycerides and sterols, including 5,8-peroxyergosterol, while the media extract was observed to contain major quantities of a single metabolite, identified as the known fungal metabolite gliovictin (1).

The isolation of gliovictin was readily accomplished by combined Sephadex (n-hexane-CH₂Cl₂-MeOH: 1:4:1) and silica (30% EtOAc-isooctane) high performance liquid chromatography. Gliovictin composed 27% of the media extract, and was identified by comparison of its physical and spectral properties with those reported [5]. Carbon-13 NMR data, which do not appear in the original literature, have been obtained for gliovictin in (CDCl₂) at 50 MHz: 165.2 s, 165.1 s, 133.9 s, 129.7 d (2C), 128.3 d (2C), 127.4 d, 73.2 s, 71.5 s, 64.1 t, 42.1 t, 30.6 q, 29.1 q, 14.0 q, 13.1 q.. The gliovictin isolated was confirmed as the originally isolated (-) isomer by comparison of its rotation, $[\alpha]_D - 62^\circ$ (c1.88, CHCl₃), with that reported (for the 3R, 6R isomer) [5] In contrast, the recently (3S, 6S), isolated from reported enantiomer Hyalodendron sp. [6], shows $[\alpha]_D + 64^\circ$. Asteromyces



| Gliovictin

cruciatus (isolate F156) was originally obtained by Dr. Paul W. Kirk from samples obtained in the lower Chesapeake Bay. We thank Dr. M. Speedie, University of Maryland, for providing this sample.

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