

[J. Antibiotics, 47, 216-224 (1994)]

[Lab. of Pharmacognosy]

Fungal Metabolites 12. Potent Immunosuppressant, 14-deoxomyriocin, (2S,3R,4R)-(E)-2-amino-3, 4-dihydroxy-2-hydroxymethyleicos-6-enoic acid and Structure-Activity Relationships of Myriocin derivatives.

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In order to investigate the structure-activity relationships, fourteen derivatives of myriocin ((2S,3R,4R)-(E)-2-amino-3,4-dihydroxy-2-hydroxymethyl-14-oxoeicos-6-enoic acid) were prepared and examined for immunosuppressive activity on mouse allogeneic mixed lymphocyte reaction in vivo. Among them, 14-deoxomyriocin was the most potent. It also suppressed the generation of allo-reactive cytotoxic T lymphocytes in mice upon intraperitoneal administration, with a potency 10-fold greater than that of myriocin.

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[Lab. of Pharmacognosy]

**Studies on the Blue Pigments Produced from Genipin and Methylamine.
I. Structures of the Brownish-red Pigments, Intermediates Leading to the Blue Pigments.**

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During the course of studies on the blue pigment formation by the reaction of genipin with methylamine, nine red to brownish-red intermediary pigments were obtained under conditions excluding oxygen. They were identified as monomer, dimer, trimer and tetramer of 2-methyl-4-carbomethoxy-2-pyridine derivatives on the basis of spectroscopic evidence.

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[Lab. of Pharmacognosy]

**Studies on the Blue Pigments Produced from Genipin and Methylamine.
II. On the formation Mechanisms of brownish-red intermediates leading to the blue pigment formation.**

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The mechanism of the formation of brownish-red pigments having a methyl-4-carbomethoxy-2-pyridine nucleus as a basic skeleton by reaction of genipin with methylamine under an atmosphere of inert gas are discussed based on the isolation of 5,6-dihydro-2-methyl-4-carbomethoxy-8-hydroxymethyl-2-pyridine as a precursor and on comparisons of the results obtained from the reactions of genipin congeners and methylamine.