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Biosynthetic Studies of Griseofulvin : Experiments using Unnatural Compounds as Substrates

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〔第21回天然有機化合物討論会 札幌 (1978年8月) で発表〕

It has been recognized that the Scheme 1 represents the biosynthetic pathway of griseofulvin. In this symposium the structural studies of the transformation products of 2'-propoxy analogues (13, 12, and 11, respectively) of griseophenone B, 4-demethyldehydrogriseofulvin, and dehydrogriseofulvin which are the genuine precursors of griseofulvin (1) will be reported. The three compounds were synthesized and each compound was incubated in the suspension of the mycelium obtained from 7-day-old cultures of *Penicillium urticae*. The products from column chromatography were analyzed by GC-MS. The results are summarized in the Scheme 4. Incubation of (12) gave three products (10), (11), and (18). The formation of (10) and (11) were expected, but (18) was unexpected product. The structure of (18) was assumed to be the enantiomer of 2'-propoxy analogue (17) of (+)-epigriseofulvin on the basis of the GC-MS data. Incubation of (13) gave (10) and (14). Similarly, incubation of (11) afforded (10) as the sole product.

Penicillium urticae is a micro-organism which produces griseofulvin as one of the metabolites. In this experiment the unnatural substances having 2'-propoxy group instead of 2'-methoxy group were used as the substrates. In the case of (12) its transformation ratio into the metabolite (10) corresponded to about one tenth of that in the tracer experiments using the natural precursor (7). This would be explained due to partly the results of the less susceptibility of the enzyme systems upon the substrate with bulky substituent at the 2'-position of the corresponding natural precursor. The formation of the metabolite (18) can be recognized as the results of the reduction mechanism from the opposite site compared with the normal biosynthetic processes.

P. urticae によるグリセオフルビンの 2'位プロポキシ同族体の生合成的生成

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〔目的〕 Griseofulvin (1) の生合成研究で, benzophenone 体(2)および demethyldehydro 体(3) からの変換についてはすでに証明されている。今回は, これらの 2' 位のプロポキシ同族体(4)および(5)が, どのような変換を受けるかに興味をもち, 本実験を行なった。