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Title	Microbial transformation of 2'-propoxy analogs of (-)- and (+)-dehydrogriseofulvin and (+)-2'-demethoxydehydrogriseofulvin by streptomyces cinereocrocatus
Sub Title	
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Publisher	共立薬科大学
Publication year	1982
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.27 (1982.), p.53-54
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000027-0053

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MICROBIAL TRANSFORMATION OF 2'-PROPOXY ANALOGS OF (-)-AND (+)-DEHYDROGRISEOFULVIN AND(+)-2'-DEMETHOXYDEHYDROGRISEOFULVIN BY STRFPTOMYCES CINEREOCROCATUS*

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In connection with the previous studies, the microbial treatment of 2'-propoxy analog of (-)-dehydrogriseofulvin (1) by S. cinereocrocatus under previously described conditions gave 4 as the reduction product and the recovered material, which were separated by silica gel column chromatography. On the other hand, the same microbial treatment of 2'-propoxy analog of (+)-dehydrogriseofulvin (2) was performed and its results were compared with those of the enantiomer (1). The results indicate that reactions of 1 proceed more rapidly that those of 2 by comparisons of the yields of the reduction product and the recovered material(s). Moreover, the comparisons of susceptibilities to microbial transformations between (-)- and (+)-dehydrogriseofulvin and their 2'-propoxy analogs indicate that the propoxy analogs are less transformed by S. cinereocrocatus. Furthermore, the relative ratios of these compounds clearly demonstrate that both substrates were transformed into the optically pure 2'-propoxy analog of (+)-griseofulvin in spite of a fact that recovered dehydrogriseofulvin analogs were a mixture of (+)- and (-)-enantiomers in the microbial treatment of 2'-propoxy analog (2) of (+)-dehydrogriseofulvin. Further, it is of importance to notice that in the microbial treatment by S. cinereocrocatus 2'-propoxy analog (2) of (+)-dehydrogriseofulvin was not transformed into the corresponding hydrogenated product (5). These results are summarized in Scheme 1.

In order to extensively elucidate the microbial transformation, (+)-2'-demethoxy-dehydrogriseofulvin (3) was synthesized as the substrate. The microbial treatment of (+)-2'-demethoxydehydrogriseofulvin (3) by *S. cinereocrocatus* for 12 hr under the same conditions described above afforded (+)-2'-demethoxygriseofulvin (6) (12%) and a mixture of (-)- and (+)-2'-demethoxy-2',3'-dihydrodehydrogriseofulvin (7 and 8), whose relative ratio was calculated as 19:81 from the value of its circular dichroism. These results are summarized in Scheme 2. Furthermore, the formation of (+)-2'-demethoxy-2',3'-dihydrodehydrogriseofulvin (8) suggests that the microorganism has the abilities of the isomerization of the substrate (3) into the enantiomer (9) and of the subsequent reduction of the latter.

Hence, we conclude that in the treatment with S. cinereocrocatus, the analogs of (-)-and (+)-dehydrogriseofulvin which have or have not substituents at 2'-position are

^{*} 本報告は Heterocycles, 17, 171 (1982) に発表.

reduced directly or after isomerization into the corresponding enantiomers, yielding (+)-and/or (-)-dihydro compound(s) as the transformation products.