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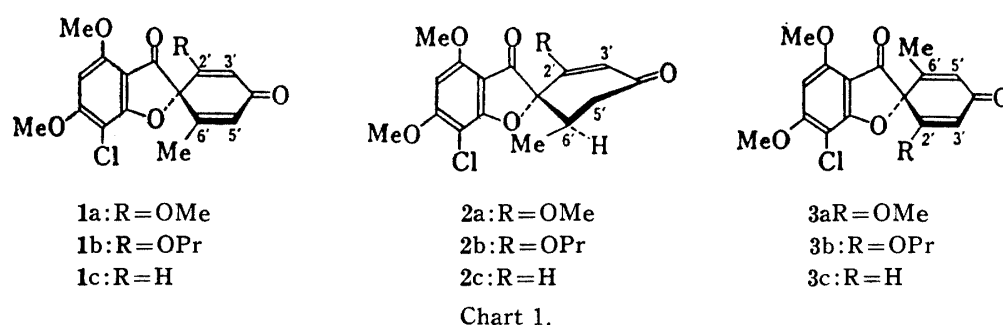
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# Microbial Transformation of (+)- and (-)-2'-Demethoxydehydrogriseofulvin by *Streptomyces cinereocrocatus*\*

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In a preceding paper we deduced by means of  $^2\text{H}$  nuclear magnetic resonance (NMR) spectroscopy that (-)- and (+)-[5'- $^2\text{H}$ ]dehydrogriseofulvin (DGF) is transformed into (+)-[5' $\alpha$ - $^2\text{H}$ ]griseofulvin (GF) by *Streptomyces cinereocrocatus*. The results of incubations of (-)- and (+)-DGF with eight *Streptomyces* species have shown that (-)- and (+)-DGF are interconvertible and are both converted to (+)-GF as the main product. Further, we have proved that the 2'-propoxy analogs (**1b** and **3b**) of (-)- and (+)-DGF were transformed into the same product, the 2'-propoxy analog (**2b**) of (+)-GF by *S. cinereocrocatus* (Chart 1).



In this communication, we describe studies which demonstrate that the microbial transformations of (+)- and (-)-2'-demethoxydehydrogriseofulvin (**1c** and **3c**) by *Streptomyces cinereocrocatus* take place directly and/or after isomerization with hydrogenations, providing further examples which indicate that the mode of the microbial transformation is greatly influenced by minor changes in the structure of substrates.

The microbial transformation of (+)- and (-)-2'-demethoxydehydrogriseofulvin (**1c** and **3c**) by *Streptomyces cinereocrocatus* was performed under the same conditions as described in the previous paper. The structures of the 12 h microbial transformation products were inferred from the  $^1\text{H}$ -NMR and mass spectral data to be (+)-2'-demethoxygriseofulvin (**6**) and a mixture of (+)- and (-)-2'-demethoxy-2',3'-dihydrodehydrogriseofulvin (**18** and **14**), whose relative ratio was calculated to be 81 : 19 by comparisons of the CD spectra with those of the standard (+)- and (-)-compounds. On the other hand, the recovered **1c** obtained after 3 h of incubation was optically pure (+)-2'-demethoxydehydrogriseofulvin without any contamination by the enantiomeric (-)-2'-demethoxydehydrogriseofulvin. Moreover, the formation of (+)-2'-demethoxy-2',3'-di-

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hydrodehydrogriseofulvin (18) suggests that the microorganism has the abilities to isomerize the substrate (1c) into the enantiomer (3c) and then to reduce the latter. Next, (–)-2'-demethoxydehydrogriseofulvin (3c) was subjected to microbial transformation by *S. cinereocrocatus*. The product, 2'-demethoxy-2',3'-dihydrodehydrogriseofulvin, was obtained in a high yield without recovery of the substrate even after 3 h. The structure was inferred from the <sup>1</sup>H-NMR and mass spectral data, and the product was confirmed to be optically pure (+)-2'-demethoxy-2',3'-dihydrodehydrogriseofulvin (18 and 14). These results are summarized in Chart 2, which indicates that the microbial hydrogenations of 1c and 3c yielded a new product reduced at the 2',3'-unsaturated bond, when compared with our previous results in the microbial transformation.

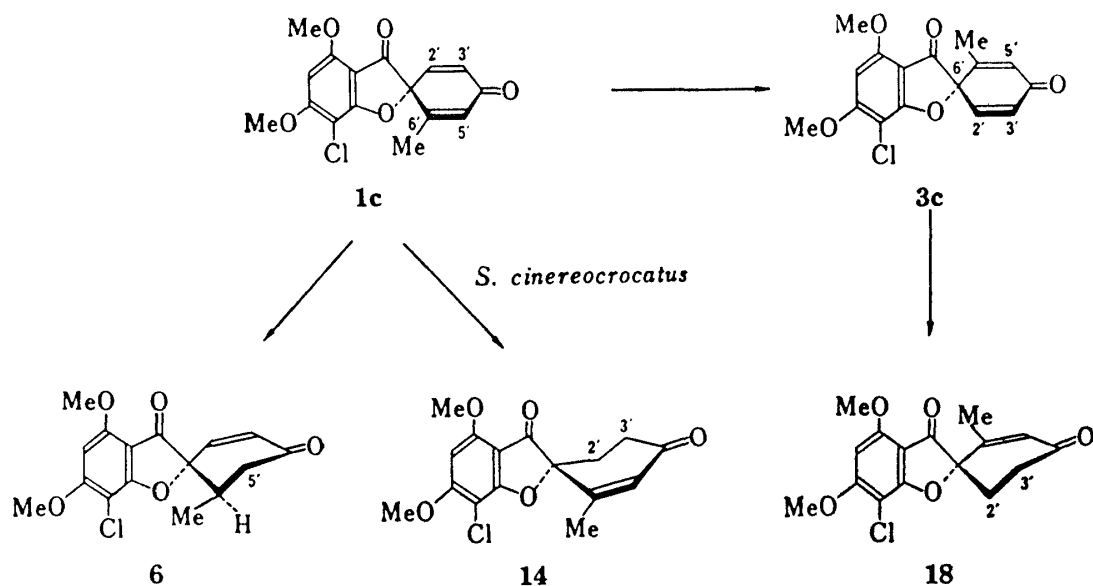


Chart 2.