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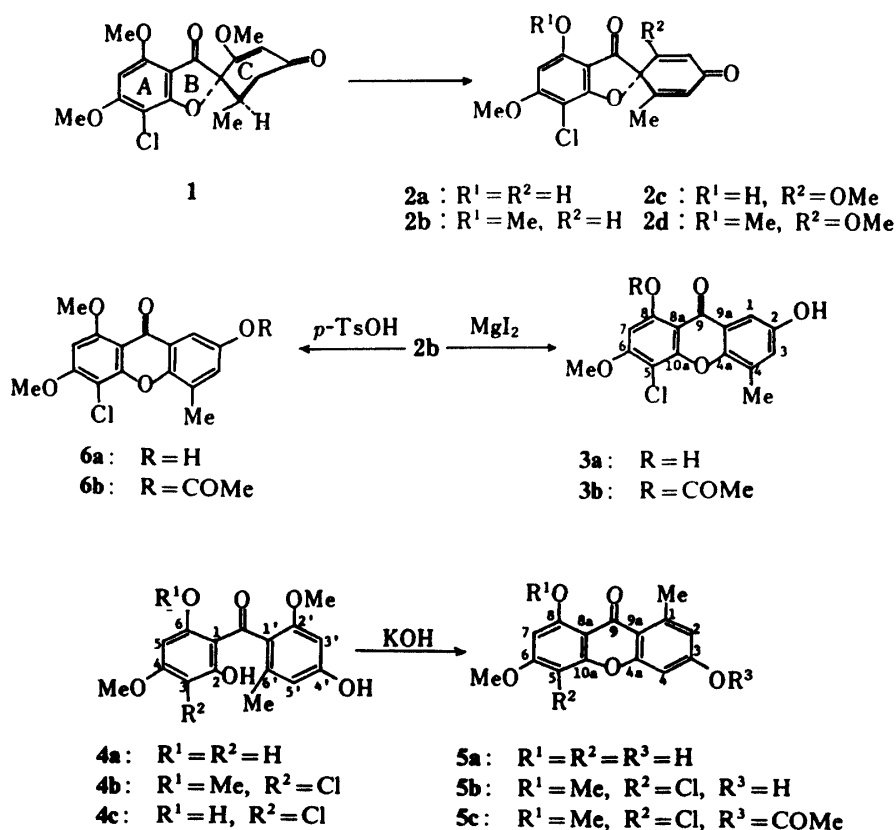
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## Dienone-Phenol Rearrangement of (+)-2'-Demethoxydehydrogriseofulvin into a 4-Methylxanthone Derivative\*

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During the course of the studies on griseofulvin biosynthesis, we attempted to prepare 2'-demethoxy-4-demethyldehydrogriseofulvin (**2a**) from **1** as a synthetic intermediate in order to examine the biosynthetic pathway in a griseofulvin-producing microorganism, *Penicillium urticae*. Treatment of (+)-2'-demethoxydehydrogriseofulvin (**2b**) with magnesium iodide afforded not the desired **2a** but a rearrangement product. For structural elucidation of the product, 3-acetoxy-5-chloro-6,8-dimethoxy-1-methylxanthone (**5c**) was synthesized from griseophenone A (3-chloro-2,2'-dihydroxy-6'-methyl-2',4,6-trimethoxybenzophenone; **4b**) as a reference compound for the  $^{13}\text{C}$ -NMR study. The structure of the rearrangement product was determined to be 5-chloro-2,8-dihydroxy-6-methoxy-4-methylxanthone (**3a**) by means of a  $^{13}\text{C}$ -NMR long-range selective proton decoupling (LSPD)



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experiment and ultraviolet and mass spectroscopic analyses, in comparison with the data for 5c. Further, treatment of 2b with p-toluenesulfonic acid caused the same rearrangement reaction except that no demethylation occurred. On the other hand, (–)-dehydrogriseofulvin (2d) was recovered unchanged after similar treatment with the acid. However, under more vigorous conditions, 2d was transformed into the racemic product.