

Title	Stereochemistry of microbial hydrogenation of (-)- α -santonin to (+)-1, 2-dihydro- α -santonin by streptomyces cinereocrocatus NRRL 3443
Sub Title	
Author	佐藤, 良博(Sato, Yoshihiro) 小田, 泰子(Oda, Taiko) 井上, 淳子(Inoue, Junko) 功刀, 正行(Kunugi, Masayuki) 鈴木, 和夫(Suzuki, Kazuo)
Publisher	共立薬科大学
Publication year	1984
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.29 (1984.) ,p.63- 64
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000029-0063

慶應義塾大学学術情報リポジトリ(KOARA)に掲載されているコンテンツの著作権は、それぞれの著作者、学会または出版社/発行者に帰属し、その権利は著作権法によって保護されています。引用にあたっては、著作権法を遵守してご利用ください。

The copyrights of content available on the KeiO Associated Repository of Academic resources (KOARA) belong to the respective authors, academic societies, or publishers/issuers, and these rights are protected by the Japanese Copyright Act. When quoting the content, please follow the Japanese copyright act.

**Stereochemistry of Microbial Hydrogenation of (–)- α -Santonin
to (+)-1,2-Dihydro- α -santonin by *Streptomyces
cinereocrocatu*s NRRL 3443***

Yoshihiro SATO, Taiko ODA, Junko INOUE, Masayuki KUNUGI**
and Kazuo T. SUZUKI**

佐藤良博, 小田泰子, 井上淳子, 功刀正行**, 鈴木和夫**

We reported the microbial transformation of (–)- and (+)-dehydrogriseofulvin and their analogs by *Streptomyces cinereocrocatu*s NRRL 3443 and it was demonstrated that hydrogenations of the dienones proceed in *trans*-diaxial manner to give the corresponding dihydro derivatives. In order to elucidate the microbial transformation activity of *S. cinereocrocatu*s, (–)- α -santonin (**1**) was selected as a cross-conjugated dienone compound. The microbial transformation of (–)- α -santonin (**1**) by *S. cinereocrocatu*s was performed under the same conditions as described in the previous paper. The mass spectrum (MS) and ^1H -NMR spectrum data indicated that the microbial transformation product might be the 1,2-dihydro derivative (**2**) of (–)- α -santonin (Chart 1). Therefore, (–)- α -santonin was partially hydrogenated over 5% palladium-charcoal catalyst in ethyl acetate to give (+)-1,2-dihydro- α -santonin (**2**). The ^1H -NMR, MS and circular dichroism (CD) data of the microbial transformation product were identical with those of **2**, demonstrating that the microbial hydrogenation of **1** by *S. cinereocrocatu*s occurs at the 1 and 2 positions. Since Inayama *et al.* have shown that **2** is in a half-chair conformation with respect to the cyclohexenone ring on the basis of the CD spectrum, which exhibited a negative CD Cotton effect, 400 MHz ^1H -NMR spectroscopy with selective proton decoupling established the assignments of all of the proton chemical shifts of (+)-1,2-dihydro- α -santonin (**2**).

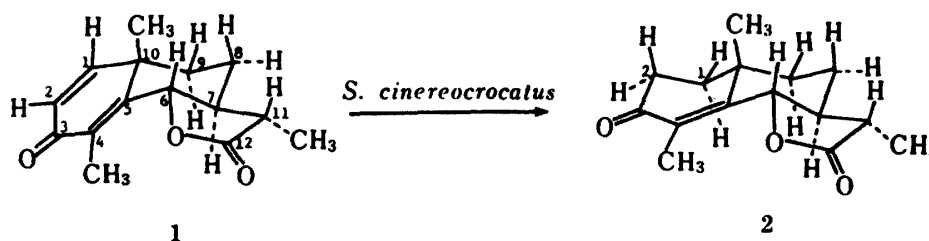


Chart 1

Consequently, to elucidate the stereochemistry of microbial hydrogenation of (–)- α -

* 本報告は *Chem. Pharm. Bull.*, **32**, 504–509 (1984) に発表

** 国立公害研究所

santonin (1) by *S. cinereocrocatu*s, the deuterated substrate, $(-)$ -[1,2- ^2H]- α -santonin (**1a**), was synthesized. Thus, the microbial transformation of $(-)$ -[1,2- ^2H]- α -santonin (**1a**) by *S. cinereocrocatu*s was performed under the same conditions as described above. The transformation product (**2a**) was proved to be deuterated $(+)$ -1,2-dihydro- α -santonin by MS and gas liquid chromatography comparisons with the standard compound (**2**). The 400 MHz ^1H -NMR spectrum of **2a** was almost identical with that of **2** except that decreases of the signal intensities at the 2α - and 1β -H regions and some differences in the 1α -, 1β -, 2α -, and 2β -H regions. Further, a coupling pattern was clearly observed at the 2β -H region, demonstrating the configurations of the deuterons of the microbial transformation product (**2a**) as 1β and 2α , respectively (Chart 2). Thus, the structure of **2a** was concluded to be $(+)$ -[1 β ,2 α - ^2H]-1,2-dihydro- α -santonin.

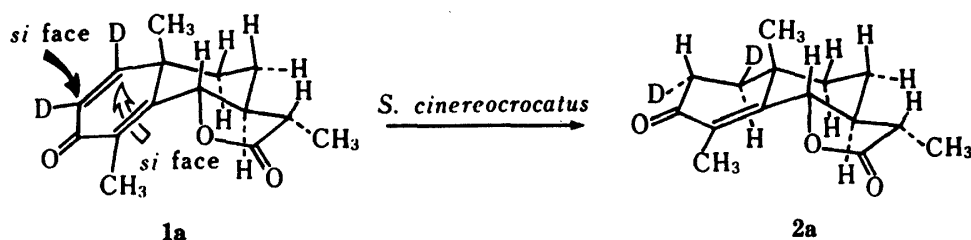


Chart 2

Comparison of the above results with those for griseofulvin derivatives indicates that the microbial hydrogenations of dienone compounds by *S. cinereocrocatu*s proceed with the same stereochemistry, *i. e.*, in a *trans* diaxial manner.