

论文

猫眼草素的结构和立体化学

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摘要:

根据生源学说、光谱分析及化学合成,将猫眼草素的原定结构A式修改为B<sub>1</sub>式。分子中氧杂环上的两个取代基互为反式,并以外消旋体(R,R+S,S)的形式存在。

关键词: 猫眼草素 香豆精新木脂素型衍生物 仿生合成

STRUCTURE AND STEREOCHEMISTRY OF MAOYANCAOSU (M-SU)

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Abstract:

Maoyancaosu (m-su), a new coumarinolignoid, was isolated from the seeds of *Euphorbia lunulata* Bge. and *Euphorbia esula* L. which are two co-occurring species with no conspicuous morphological differences. Biogenetic considerations and spectroscopic analysis (NMR, MS, IR) led to the revision of the original structure (A) of m-su to (B<sub>1</sub>). The new structure (B<sub>1</sub>) was confirmed by synthesis and comparison of relevant data (mp, Rf, IR). The two substituents at C-1' and C-2' of the dioxane ring in m-su were found to be equatorial and trans to each other from the coupling constant (8Hz) of the two axial hydrogens. It is devoid of any optical activity (589—365 nm) and hence a racemic mixture (R,R+S,S). In our hands the silver oxide for the coupling of I and II was used in ten-fold excess in order to achieve a moderate yield, in contrast with the equimolar quantity reported in the literature. It is of interest to note that the unnatural isomer (III<sub>2</sub>, 32%) was actually obtained in much higher yield in the biomimetic synthesis at the expense of the natural one (III<sub>1</sub>, 10%), apparently because of the reluctance of the electron-poor 7-OH (as compared with 6-OH) of esuletin (II) in parting with an electron to form the required free radical. In the plant, esculin (6-glucoside of II) or its equivalent is probably involved in the biogenetic pathway, where blocking of the 6-OH will account for the occurrence of m-su (B<sub>1</sub>) as the exclusive isomer.

Keywords: Coumarinolignoid Biomimetic synthesis Maoyancaosu

收稿日期 1982-12-13 修回日期 网络版发布日期

DOI:

基金项目:

通讯作者:

作者简介:

参考文献:

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