

REVISED STRUCTURE AND STEREOCHEMISTRY OF CHRYSARTEMIN B

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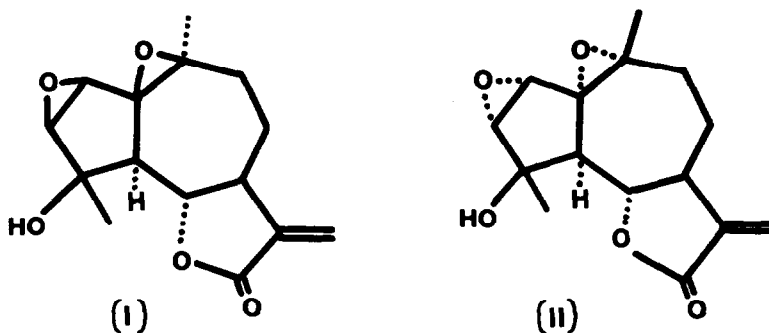
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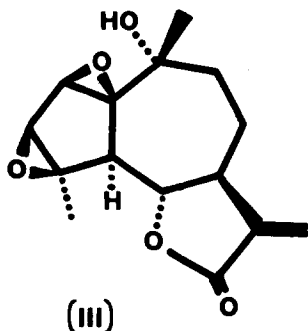
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During the course of our search for rooting promoters in *Chrysanthemum morifolium* Ram. c.v. 'Otomezakura', we have isolated chrysartemins A and B¹, and chlorochrymorin² as the active principles together with chrysandiol³. Chrysartemins A and B were first reported in 1970 by Romo *et al*⁴ and were assigned structures I and II respectively on the basis of i.r., n.m.r. and mass spectral and chemical evidences.



However, reexamination of the physical properties of chrysartemin B has cast doubts on the validity of the assigned structure II. In order to unambiguously establish the structure and stereochemistry we have undertaken the single crystal X-ray crystallographic analysis of chrysartemin B.

A single crystal of chrysartemin B ($C_{15}H_{18}O_5$), obtained by recrystallization from *n*-hexane-ethyl acetate, was shown to belong to the orthorhombic space group $P2_12_12_1$ with $a=14.371$, $b=16.049$, $c=5.853\text{\AA}$, and $Z=4$. A total of 871 independent reflections with $I>3\sigma(I)$, whose intensity data were measured on a Rigaku four-circle diffractometer using Mo-K α radiation, were used in the solution and refinement. The data were corrected for Lorentz and polarisation factors, but not for absorption. The structure was solved by direct methods (MULTAN 74)⁵ and refined by block-diagonal least squares method. All twenty non-hydrogen atoms were initially assumed to be carbon atoms with the five oxygen atoms being assigned subsequently on the basis of bond lengths and temperature factors. All hydrogen atoms were located by difference Fourier syntheses. Refinement with anisotropic temperature factors for the carbon and oxygen atoms is in progress, the *R* factor at the present stage being 0.046. The absolute stereochemistry has not been established. Hence, the molecular structure of chrysartemin B is III or its mirror image. All bond lengths and interbond angles were as expected (Fig.1) and the three-dimensional structure is illustrated in Fig.2.



All guaianolides in which the α -methylene- γ -lactone chromophore has the C-7 side chain β -oriented and is *trans*-fused at C-6, exhibit a negative Cotton effect⁶. The structure of chrysartemin B shows *trans*-fusion at C-6 and C-7 of the α -methylene- γ -lactone moiety and coupled with the strong negative Cotton effect in the CD spectrum at 254nm ($\theta=-2980$, methanol), would suggest the absolute stereochemistry of chrysartemin B is III. Chrysartemin B is the stereoisomer of canin⁷, which was isolated from *Artemisia cana* subsp. *cana*.

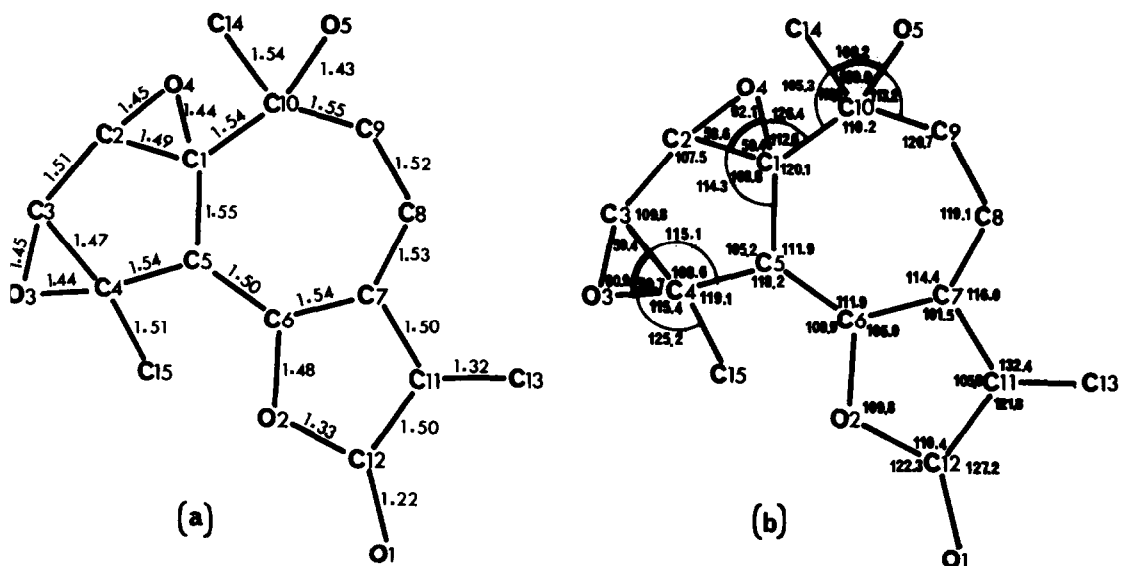


Fig.1. (a) Bond lengths (Å) and (b) bond angles (°) in chrysartemin B.

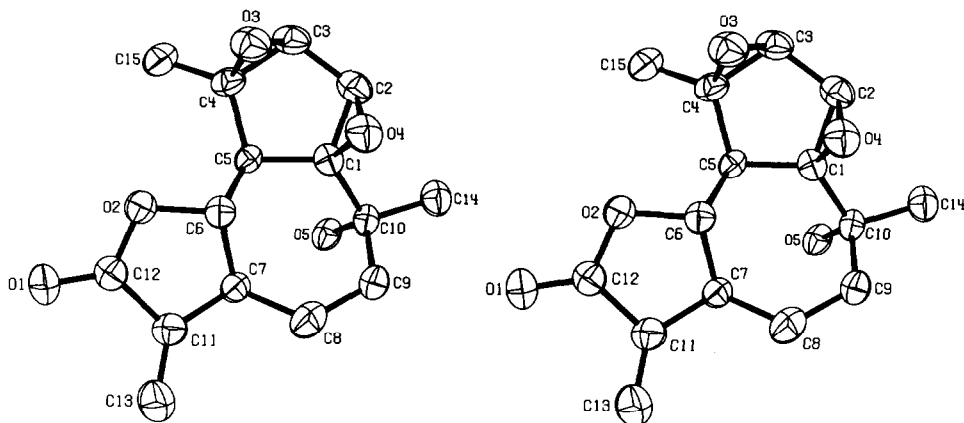


Fig.2. Stereoscopic view of chrysartemin B showing thermal ellipsoids of 50% probability. The hydrogen atoms have been omitted for clarity.

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