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(±)-6-*epi*-Eriolanin

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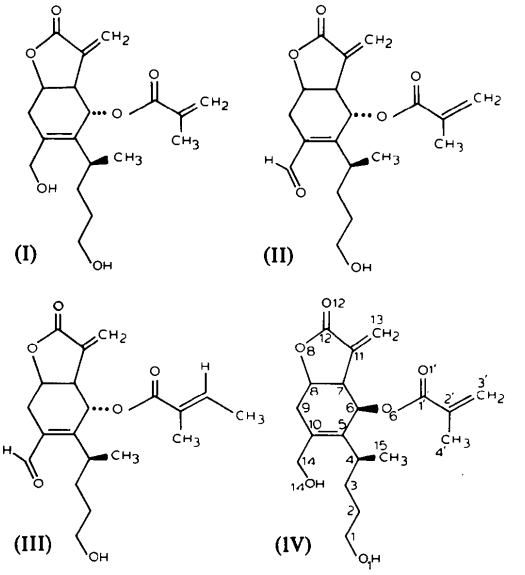
Abstract. $C_{19}H_{26}O_6$, monoclinic, $P2_1/c$, a = 9·4729 (6), b = 12·064 (1), c = 16·426 (2) Å, β = 97·60 (1)°, V = 1860·7 Å^3, ρ_o = 1·26 (by flotation), ρ_c = 1·25 Mg m^{-3} (for Z = 4). The structure determination was undertaken to establish the relative stereochemistry at the 6-position of this synthetic analog of eriolanin. Relative to the bicyclic ring system of the closely related dehydroeriolanin, epimerization at the 6-position causes an *endo* to *exo* conformational flip of the 1,4-diplanar (boat) cyclohexene ring. The structure has been refined to a residual of R = 0·064 for 2229 observable data measured with copper radiation.

Introduction. Eriolanin (I) is a naturally occurring antileukemic 1,10-secoeudesmanolide isolated from *Eriophyllum lanatum* Forbes (Compositae) by Kupchan, Baxter, Chiang, Gilmore & Bryan (1973). Structural elucidation of eriolanin was by a combination of spectral and X-ray diffraction studies, the latter work performed by Bryan & Gilmore (1975). They studied a mixed crystal of dehydroeriolanin (DE, II) and dehydroeriolangin (III) in which the two eudesmanolides had co-crystallized. As part of a search for analogs of natural products with anti-leukemic properties, one of us (PAG) synthesized the 6-epimer of



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eriolanin (6-EE; IV; Grieco, Oguri, Gilman & DeTitta, 1978). NMR spectral data were not readily interpretable and in order to firmly establish the relative stereochemistry of the 6-position a single-crystal diffraction experiment was undertaken.

Intensity data were measured on a columnar crystal of approximate dimensions 0·08 × 0·12 × 0·60 mm. Of 3804 independent reflections measured on a CAD-4 diffractometer with a copper source and using a variable scan width of $(0{\cdot}8 + 0{\cdot}14 \tan\theta)°$ in the $\theta/2\theta$ mode, 2229 were considered observable ($I > 2\sigma_I$) and these were used for the refinement of the structural model. Intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu_{Cu} = 0{\cdot}77$ mm^{-1}). The structure was determined by multi-solution tangent formula techniques (Germain, Main & Woolfson, 1971) and refined by a least-squares procedure to a conventional residual of $R = 0{\cdot}064$ and a weighted residual of $R_w = 0{\cdot}087$. Scattering factors for O and C used in the refinement were those of Cromer & Waber (1974) and for H those of Stewart, Davidson & Simpson (1965). The weighting scheme employed was as described by eq. H14 of Stout & Jensen (1968) except that $0{\cdot}01N_{pk}$ was replaced by $0{\cdot}05N_{pk}$.

Table 1. *Atomic positional parameters and estimated standard deviations* (×10⁴) *of* (±)-6-*epi-eriolanin*

	x	*y*	*z*
C(1)	5461 (4)	3224 (3)	6640 (2)
C(2)	5801 (4)	2645 (3)	5869 (2)
C(3)	5924 (3)	3432 (2)	5158 (2)
C(4)	6094 (3)	2864 (3)	4346 (2)
C(5)	4794 (3)	2180 (2)	4028 (2)
C(6)	3387 (3)	2781 (2)	3892 (2)
C(7)	2573 (3)	2517 (3)	3050 (2)
C(8)	2451 (3)	1248 (3)	2919 (2)
C(9)	3347 (3)	546 (3)	3544 (2)
C(10)	4766 (3)	1090 (2)	3850 (2)
C(11)	1056 (3)	2888 (3)	2948 (2)
C(12)	145 (4)	1906 (3)	2924 (3)
C(13)	508 (4)	3880 (4)	2904 (3)
C(14)	6028 (4)	328 (3)	3951 (2)
C(15)	6388 (4)	3730 (3)	3696 (2)
C(1′)	1861 (3)	3189 (3)	4928 (2)
C(2′)	803 (4)	2691 (3)	5413 (2)
C(3′)	0 (4)	3422 (4)	5773 (3)
C(4′)	622 (5)	1490 (4)	5459 (3)
O(1)	6480 (3)	4024 (2)	6946 (2)
O(6)	2486 (2)	2409 (2)	4500 (1)
O(8)	941 (2)	985 (2)	2935 (2)
O(12)	−1132 (3)	1858 (3)	2894 (2)
O(14)	6064 (3)	−388 (2)	3265 (1)
O(1′)	2111 (3)	4156 (2)	4891 (2)

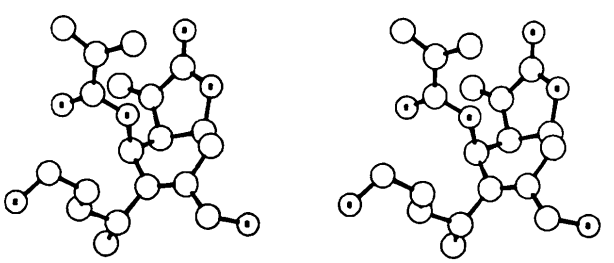


Fig. 1. A stereoview of 6-*epi*-eriolanin.

Discussion. A stereoview of the molecule is shown in Fig. 1. Non-hydrogen positional parameters are listed in Table 1; bond distances, bond angles, and torsion angles are given in Fig. 2. A view of the crystal packing is shown in Fig. 3.*

In their study of dehydroeriolanin, Bryan & Gilmore (1975) noted that the bicyclic moiety of DE had a 1,4-diplanar (boat) cyclohexene ring conformation. The form is *endo*; *i.e.* the C(5)=C(10) bond is directed in towards the lactone ring. The *endo* conformation

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34357 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

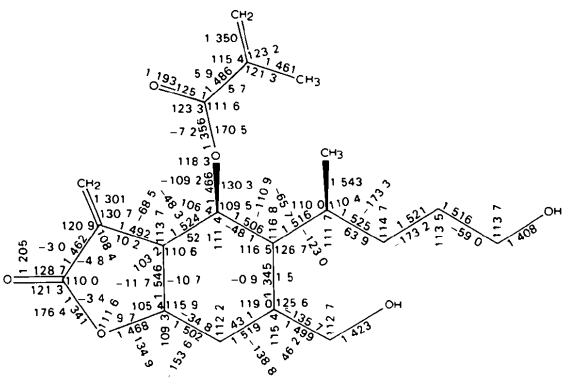


Fig. 2. Bond distances (Å), bond angles (°) and torsion angles (°) for 6-*epi*-eriolanin. Average e.s.d.'s for distances, angles, and torsion angles are 0·005 Å, 0·2° and 0·3° respectively. Positive torsion angles refer to clockwise rotations of back bonds with respect to stationary front bonds when looking down the middle bond.

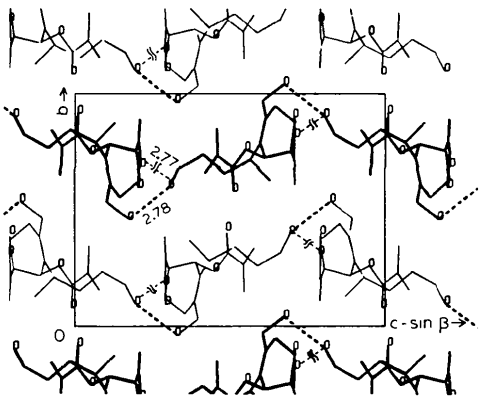
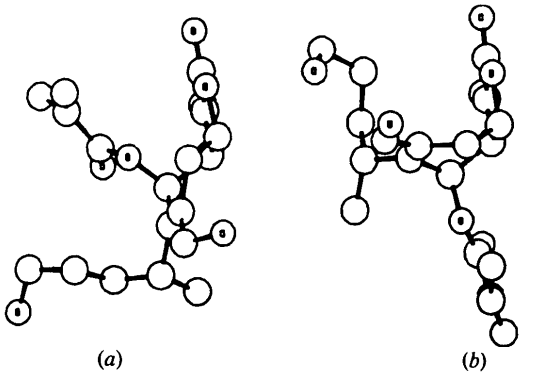


Fig. 3. View of the crystal packing of 6-*epi*-eriolanin down the crystallographic *a* axis. The hydrogen bonds O(14)H···O(1)H···O(12) link molecules into sheets normal to *b*.



(*a*) (*b*)

Fig. 4. Side-by-side views of (*a*) 6-*epi*-eriolanin and (*b*) dehydroeriolanin (Bryan & Gilmore, 1975). The lactone rings and atoms C(6) and C(9) have been oriented similarly by a least-squares fitting procedure. Note that the 6-methacrylate chains are oriented axially on both epimers but in opposite directions *vis à vis* the common lactone-ring orientations.

directs the C(6) methacrylate group to the pseudo-axial position. In this study we again observe a 1,4-diplanar cyclohexene ring conformation; however, in this case the form is *exo*; *i.e.* C(5)=C(10) is directed away from the lactone ring. This ring flip causes the methacrylate group to assume again the pseudo-axial position. Side views of 6-*epi*-eriolanin and DE are shown in Fig. 4. The views were constructed by orienting the 6-*epi*-eriolanin molecule in such a way as to emphasize the *exo* conformation of the bicyclic ring and show the disposition of the side groups at C(6), C(5), and C(10) relative to it. The view of DE was derived from that of 6-EE by a least-squares fitting of the lactone ring and atoms C(13), C(6), C(9) of DE to the corresponding atoms of 6-EE.

Inspection of Fig. 4 indicates that epimerization at C(6) has occasioned a rather dramatic conformational isomerization of the sesquiterpene lactone ring system, with an attendant relocation of biologically important functional groups at C(5) and C(10) *vis à vis* a fixed lactone position. It explains the difficulty in the interpretation of the PMR spectrum of 6-EE in the H(6) area since epimerization did not affect the coupling of H(6) as expected. Modeling indicates that the isomerization upon epimerization is due to crowding by the C(13) methylene and C(15) methyl which would result if epimerization were to occur without isomerization.

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cis-[1,2;3,4;5,6]-Triiminocyclohexane (*cis*-Benzene-Trisimine)

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Abstract. $C_6H_9N_3$, $M_r = 123{\cdot}18$, monoclinic, $P2_1/c$, $a = 8{\cdot}561\ (5)$, $b = 10{\cdot}656\ (4)$, $c = 6{\cdot}569\ (5)$ Å, $\beta = 107{\cdot}70\ (3)°$, $V = 570{\cdot}89\ (16)$ Å^3, $Z = 4$, $D_m = 1{\cdot}44\ (1)$, $D_c = 1{\cdot}43$ Mg m^{-3}. λ(Mo $K\bar{\alpha}$) = 0·71073 Å, μ(Mo $K\bar{\alpha}$) = 0·1017 mm^{-1}, $F(000) = 264$. The structure was solved by the symbolic-addition procedure and refined to $R = 0{\cdot}040$ for the 1665 observed reflexions. The molecule is asymmetric, the three aziridine rings show an outward tilt. The six-membered ring is nearly planar. Two of the three amino protons show strong

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