

(Spek, 1993). Data collection and reduction and cell refinement: *CAD-4/PC* software (Enraf-Nonius, 1989). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1093). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7 β ,8 β -Epoxyfriedelane

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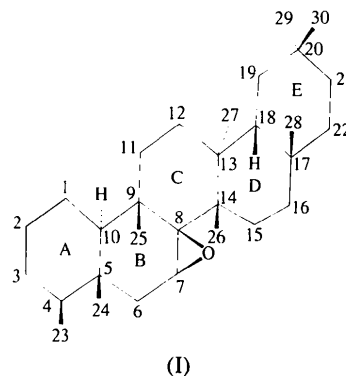
Abstract

The title compound, $C_{30}H_{50}O$, was produced by a series of chemical reactions from the parent compound putranjivadiene which is obtained as a natural product from *Putranjiva roxburghii* (Euphorbiaceae), a plant common to tropical India and used against fever and cold. The molecular structure consists of five fused six-membered alicyclic rings with a β -oriented O atom bridging the C7 and C8 atoms. The molecule as a whole assumes nearly buckled semi-circular geometry.

Comment

Putranjiva roxburghii (Euphorbiaceae) is a common plant in tropical India, the leaves and fruits (Chopra, Nayar & Chopra, 1956) of which are used as indigenous medicine against cold and fever. The neutral material from the benzene extract of the whole plant (Sengupta, Chakraborty, Duffield, Durham &

Djerass, 1968) yielded two crystalline compounds from chromatography over activated alumina, of which the less polar component was identical to friedelin and the more polar constituent (m.p. 557–562 K), having the molecular formula $C_{30}H_{48}O_2$ (molecular weight 440 by MS), was named putranjivadiene, which, along with its derivatives, was found to possess a friedelane nucleus (Sengupta, Chakraborty, Duffield, Durham & Djerass, 1968; Courtney & Shannon, 1963; Shannon, McDonald & Courtney, 1963). The present compound was obtained by a series of chemical reactions from the parent compound putranjivadiene. The three-dimensional structure determination of the title compound (I) was undertaken as part of our programme aimed at characterizing the conformation of this series of compounds which has promise for drug use. The determination was also useful for understanding the reaction mechanism involved in the olefin stereochemistry and the structural basis of the synthesis of this natural product. The possible antitumor activity of the epoxide group of compounds has been investigated in other laboratories (Read & Vining, 1963; Marumo, Sasaki & Suzuki, 1964).



Several natural products possess the 2,3-epoxy-4-quinol structure (Closse, Mauli & Sigg, 1966; Brodasky, Stroman, Dietz & Mizesak, 1983; Box, Gilpin, Gwynn, Hanscomb, Spear & Brown, 1983; Read & Vining, 1963; Marumo, Sasaki & Suzuki, 1964). Mycochryson, a metabolite discomycete, and cervicarcin, both antitumor agents produced by *Streptomyces ogaensis*, are typical examples (Read & Vining, 1963; Marumo, Sasaki & Suzuki, 1964). Previous investigations on the cytotoxic limonoids from the Himalayan Meliaceae species, *Aphanamixis graddifolia* BI, have shown that when an intact steroid D-ring system bearing a 14 β ,15 β -epoxide is replaced by the product of rearrangement, namely a 15-oxo system, it becomes marginally inactive (Kamano, Pettit, Inoue, Tozawa & Komeichi, 1977). Apparently, the 14,15 β epoxide is a very definite requirement for inhibition of neoplastic (P 338) cell

growth. This is reminiscent of an analogous structural modification and loss of activity observed with compounds of the bufadienolide type (Kamano, Pettit, Inoue, Tozawa & Komeichi, 1977). These findings suggest that the introduction of a 14,15 β -epoxide function in an inactive tetracyclic triterpene might lead to a cytotoxic compound (Merrien, Meunier, Pascard & Polonsky, 1981). Very few X-ray structural studies have been carried out on epoxides of the friedelane series, though the structure of friedelin has been solved (Declercq, Puyvelde, Kimpe, Nagy, Verhegge & Vierman, 1991; Mo, Winther & Scrimgeour, 1989) and our molecular chirality matches this structure. The present molecule consists of five six-membered alicyclic fused rings in a friedelane structure with a β -oriented epoxy O atom bridging the C7 and C8 atoms. The C27 and C29 atoms of the methyl side chains are α -oriented. The methyl C23, C24, C25, C26, C28 and C30 atoms and the epoxy O atom are β -oriented with respect to the mean plane of the molecule.

An ORTEP (Johnson, 1965) plot showing the H atoms and the atom labelling is presented in Fig. 1.

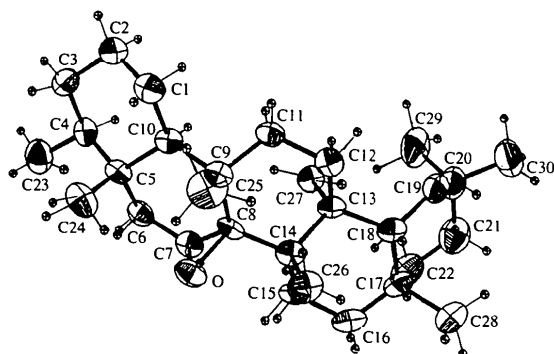


Fig. 1. An ORTEP plot (Johnson, 1965) of the title molecule showing the H atoms and the labelling scheme used in the tables. Displacement ellipsoids are at the 50% probability level.

Experimental

Crystal data

C₃₀H₅₀O

$M_r = 426.70$

Monoclinic

$P2_1$

$a = 7.804 (1) \text{ \AA}$

$b = 11.754 (2) \text{ \AA}$

$c = 14.443 (2) \text{ \AA}$

$\beta = 103.57 (2)^\circ$

$V = 1287.90 (3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.10 \text{ Mg m}^{-3}$

$D_m = 1.12 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54182 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 25\text{--}30^\circ$

$\mu = 0.443 \text{ mm}^{-1}$

$T = 300 \text{ K}$

Needle

$0.28 \times 0.21 \times 0.18 \text{ mm}$

White

Crystal source: putranjivadione (a medicinal plant extract)

Data collection

Enraf-Nonius CAD-4

diffractometer

ω - 2θ scans

Absorption correction:

none

1859 measured reflections

1614 independent reflections

1403 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.069$

$\theta_{\text{max}} = 55^\circ$

$h = -12 \rightarrow 12$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 16$

3 standard reflections

monitored every 100

reflections

intensity variation: none

Refinement

Refinement on F

$R = 0.064$

$wR = 0.062$

$S = 1.855$

1403 reflections

280 parameters

Only coordinates of H atoms

refined

$w = 1/[\sigma^2(F)$

$+ 0.025224F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.75$

$\Delta\rho_{\text{max}} = 0.261 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.250 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

	x	y	z	B_{eq}
C1	-0.1500 (8)	0.1789	-0.1120 (4)	4.0 (2)
C2	-0.2914 (7)	0.2532 (8)	-0.1754 (4)	4.4 (2)
C3	-0.2291 (8)	0.2996 (9)	-0.2588 (4)	4.5 (2)
C4	-0.0544 (7)	0.3623 (7)	-0.2263 (4)	3.4 (1)
C5	0.0917 (7)	0.2858 (7)	-0.1652 (3)	2.8 (1)
C6	0.2474 (7)	0.3629 (7)	-0.1253 (4)	3.6 (2)
C7	0.3772 (7)	0.3246 (7)	-0.0384 (4)	3.4 (1)
C8	0.3394 (6)	0.2381 (7)	0.0284 (4)	2.5 (1)
C9	0.1559 (7)	0.1799 (7)	0.0047 (4)	2.7 (1)
C10	0.0258 (6)	0.2425 (6)	-0.0785 (4)	2.8 (1)
C11	0.0707 (7)	0.1859 (7)	0.0921 (4)	3.4 (1)
C12	0.1933 (7)	0.1769 (7)	0.1896 (4)	3.4 (1)
C13	0.3455 (6)	0.2646 (7)	0.2051 (4)	2.7 (1)
C14	0.4563 (7)	0.2357 (5)	0.1317 (4)	3.2 (1)
C15	0.6079 (7)	0.3207 (8)	0.1469 (4)	3.8 (2)
C16	0.7293 (7)	0.3111 (9)	0.2445 (5)	4.6 (2)
C17	0.6454 (7)	0.3102 (8)	0.3304 (4)	4.1 (2)
C18	0.4574 (7)	0.2551 (7)	0.3076 (4)	3.2 (1)
C19	0.3622 (8)	0.2816 (8)	0.3890 (4)	4.1 (2)
C20	0.3784 (10)	0.3993 (9)	0.4398 (5)	5.4 (2)
C21	0.5629 (12)	0.4416 (9)	0.4532 (5)	6.1 (3)
C22	0.6391 (9)	0.4331 (8)	0.3664 (6)	5.3 (2)
C23	-0.0045 (9)	0.4188 (9)	-0.3137 (5)	5.5 (2)
C24	0.1451 (9)	0.1893 (8)	-0.2250 (5)	4.5 (2)
C25	0.1775 (9)	0.0526 (7)	-0.0192 (5)	4.8 (2)
C26	0.5371 (8)	0.1142 (8)	0.1465 (5)	4.6 (2)
C27	0.2616 (7)	0.3835 (7)	0.1812 (4)	3.1 (2)
C28	0.7674 (9)	0.2402 (9)	0.4100 (5)	5.5 (2)
C29	0.2482 (12)	0.4871 (10)	0.3886 (6)	7.4 (3)
C30	0.3366 (11)	0.3776 (12)	0.5361 (5)	7.9 (3)
O	0.4445 (5)	0.2104 (6)	-0.0392 (3)	4.1 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C2—C1	1.531 (8)	C8—O	1.452 (7)
C2—C3	1.503 (10)	C7—C6	1.486 (8)
C10—C1	1.537 (7)	C7—O	1.442 (10)
C10—C5	1.547 (8)	C11—C12	1.508 (7)
C10—C9	1.563 (8)	C12—C13	1.548 (9)
C5—C4	1.554 (9)	C13—C14	1.557 (9)
C5—C6	1.517 (9)	C13—C18	1.537 (7)
C5—C24	1.541 (12)	C13—C27	1.546 (11)
C4—C3	1.524 (9)	C14—C15	1.525 (10)

C4—C23	1.555 (10)	C14—C26	1.555 (12)	Closse, A., Mauli, R. & Sigg, H. P. (1966). <i>Helv. Chim. Acta</i> , 49 , 204–208.
C9—C8	1.551 (8)	C18—C17	1.566 (8)	Courtney, J. L. & Shannon, J. S. (1963). <i>Tetrahedron Lett.</i> pp. 13–20.
C9—C11	1.563 (9)	C18—C19	1.562 (9)	Declercq, J.-P., Puyvelde, L. V., Kimpe, N. D., Nagy, M., Verhegge, G. & Vierman, R. D. (1991). <i>Acta Cryst.</i> C47 , 209–211.
C9—C25	1.554 (11)	C17—C16	1.533 (10)	Johnson, C. K. (1965). <i>ORTEP</i> . Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
C8—C7	1.478 (10)	C17—C22	1.540 (13)	Kamano, Y., Pettit, G. R., Inoue, M., Tozawa, M. & Komeichi, J. (1977). <i>J. Chem. Res. (M)</i> , pp. 840–845.
C8—C14	1.556 (7)	C17—C28	1.546 (10)	Marumo, S., Sasaki, K. & Suzuki, S. (1964). <i>J. Am. Chem. Soc.</i> 86 , 4507–4508.
C16—C15	1.507 (8)	C20—C29	1.514 (14)	Merrien, A., Meunier, B., Pascard, C. & Polonsky, J. (1981). <i>Tetrahedron</i> , 37 , 2303–2306.
C19—C20	1.557 (13)	C20—C30	1.523 (11)	Mo, F., Winther, S. & Scrimgeour, S. N. (1989). <i>Acta Cryst.</i> B45 , 261–270.
C20—C21	1.492 (12)	C21—C22	1.512 (12)	Read, G. & Vining, L. C. (1963). <i>Chem. Ind. (London)</i> , pp. 1239–1244.
C1—C2—C3	111.3 (5)	C12—C13—C27	107.5 (4)	Sengupta, P., Chakraborty, A. K., Duffield, A. M., Durham, L. J. & Djerass, C. (1968). <i>Tetrahedron</i> , 24 , 1205–1213.
C1—C10—C9	112.6 (4)	C12—C13—C18	109.6 (5)	Shannon, J. S., McDonald, C. G. & Courtney, J. L. (1963). <i>Tetrahedron Lett.</i> pp. 173–179.
C1—C10—C5	110.3 (4)	C12—C13—C14	106.7 (5)	Sheldrick, G. M. (1976). <i>SHELX76. Program for Crystal Structure Determination</i> . Univ. of Cambridge, England.
C2—C1—C10	112.1 (4)	C18—C13—C27	113.3 (5)	Sheldrick, G. M. (1985). <i>SHELXS86. Program for the Solution of Crystal Structures</i> . Univ. of Göttingen, Germany.
C2—C3—C4	111.3 (5)	C14—C13—C27	108.5 (5)	
C5—C10—C9	119.8 (4)	C14—C13—C18	110.9 (4)	
C6—C5—C24	110.8 (5)	C8—C14—C13	110.7 (4)	
C4—C5—C24	111.5 (4)	C13—C14—C26	112.3 (5)	
C4—C5—C6	106.6 (5)	C13—C14—C15	107.3 (5)	
C5—C4—C23	114.7 (5)	C8—C14—C26	106.0 (5)	
C5—C4—C3	112.3 (6)	C8—C14—C15	112.8 (5)	
C3—C4—C23	109.4 (5)	C15—C14—C26	107.8 (5)	
C7—C8—O	59.0 (4)	C13—C18—C19	116.4 (5)	
C7—C8—C14	118.4 (5)	C13—C18—C17	117.8 (5)	
C8—C7—O	59.0 (4)	C17—C18—C19	110.3 (5)	
C8—C7—C6	124.0 (5)	C18—C17—C28	108.6 (6)	
C6—C7—O	116.9 (5)	C18—C17—C22	110.9 (5)	
C5—C6—C7	117.8 (6)	C18—C17—C16	112.9 (5)	
C9—C11—C12	117.1 (5)	C22—C17—C28	108.1 (6)	
C8—C9—C25	109.3 (5)	C16—C17—C28	107.4 (5)	
C8—C9—C11	110.4 (5)	C16—C17—C22	108.7 (6)	
C9—C8—O	113.0 (5)	C17—C16—C15	117.6 (5)	
C9—C8—C14	120.5 (5)	C14—C15—C16	112.4 (6)	
C9—C8—C7	118.3 (5)	C18—C19—C20	122.1 (6)	
C10—C5—C24	113.4 (5)	C19—C20—C30	105.7 (8)	
C10—C5—C6	106.1 (4)	C19—C20—C29	113.9 (6)	
C10—C5—C4	108.1 (4)	C19—C20—C21	109.0 (7)	
C10—C9—C25	111.5 (5)	C29—C20—C30	107.3 (7)	
C10—C9—C11	106.1 (5)	C21—C20—C30	110.1 (6)	
C10—C9—C8	111.2 (5)	C21—C20—C29	110.7 (8)	
C11—C9—C25	108.2 (5)	C20—C21—C22	115.2 (7)	
C14—C8—O	110.1 (4)	C17—C22—C21	113.1 (7)	
C11—C12—C13	112.6 (5)	C8—O—C7	61.4 (4)	

The structure was solved with *SHELXS86* (Sheldrick, 1985) using 282 *E* values ($E > 1.20$) which revealed all the 31 non-H atoms. The structure was refined by least-squares methods using *SHELX76* (Sheldrick, 1976). All 50 H atoms were located from a difference Fourier map and positioned with ideal geometry and held fixed for the final refinement of the 31 heavy atoms with anisotropic displacement parameters which led to a final *R* index ($(\sum ||F_o| - |F_c|| / \sum |F_o|)$) of 0.064.

The authors are thankful to CSIR Government of India for financial help.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, torsion angles, intermolecular contacts less than 3.60 Å and ring-puckering coordinates have been deposited with the IUCr (Reference: AL1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Piperidine Nitroxide Radicals with Heterocyclic Ring Substituents. 4-Hydroxy-2,2,6,6-tetramethyl-4-(2-pyridylmethyl 1-oxide)piperidine 1-Oxide

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Abstract

In the title compound, $C_{15}H_{23}N_2O_3$, an intramolecular hydrogen bond between the hydroxyl group and the O atom of the 2-pyridylmethyl 1-oxide substituent results in a seven-membered ring which shows a twist-chair conformation.

Comment

A perspective view of the molecule showing the atom-numbering scheme and the intramolecular hydrogen bond is given in Fig. 1.