Refinement

Refinement on F
$R = 0.0425$
$wR = 0.057$
$S = 0.97$
2330 reflections
248 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F) + 0.00395F^2]$
$(\Delta/\sigma)_{\max} = 0.3$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
Molecule (I)				
O1	0.80587 (9)	0.0451 (1)	−0.05992 (7)	3.68 (3)
C1	0.8811 (2)	0.1869 (2)	−0.0707 (1)	3.64 (4)
C2	0.9389 (1)	0.2719 (2)	0.00570 (9)	2.99 (3)
N1	1.0495 (1)	0.2413 (2)	0.04599 (7)	3.26 (3)
C3	1.0634 (1)	0.3424 (2)	0.11368 (9)	3.06 (3)
C4	0.9568 (1)	0.4329 (2)	0.11275 (9)	3.16 (3)
N2	0.8789 (1)	0.3850 (2)	0.04297 (1)	3.15 (3)
C5	0.9444 (2)	0.5403 (2)	0.1747 (1)	4.14 (4)
C6	1.0436 (2)	0.5567 (3)	0.2371 (1)	4.63 (4)
C7	1.1522 (2)	0.4701 (2)	0.2378 (1)	4.31 (4)
C8	1.1640 (1)	0.3637 (2)	0.1763 (1)	3.87 (4)
Molecule (II)				
O21	0.3368 (1)	0.0119 (2)	−0.04423 (8)	4.12 (3)
C21	0.3126 (2)	0.1926 (2)	−0.0541 (1)	3.65 (4)
C22	0.3815 (1)	0.2983 (2)	0.01385 (9)	3.13 (3)
N21	0.4887 (1)	0.2441 (2)	0.05828 (8)	3.40 (3)
C23	0.5277 (1)	0.3689 (2)	0.11477 (9)	3.19 (3)
C24	0.4382 (1)	0.4976 (2)	0.10114 (9)	3.29 (3)
N22	0.3468 (1)	0.4486 (2)	0.03662 (8)	3.41 (3)
C25	0.4484 (2)	0.6415 (3)	0.1508 (1)	4.37 (4)
C26	0.5476 (2)	0.6501 (3)	0.2136 (1)	4.73 (5)
C27	0.6369 (2)	0.5202 (3)	0.2262 (1)	4.35 (4)
C28	0.6291 (1)	0.3787 (2)	0.1767 (1)	4.05 (4)

Table 2. *Selected geometric parameters* (Å, °)

Molecule (I)		Molecule (II)	
O1—C1	1.423 (2)	O21—C21	1.414 (2)
C1—C2	1.491 (2)	C21—C22	1.498 (2)
C2—N1	1.316 (2)	C22—N22	1.309 (2)
C2—N2	1.359 (2)	C22—N21	1.353 (2)
N1—C3	1.388 (2)	N21—C23	1.370 (2)
C3—C4	1.398 (2)	C23—C24	1.400 (2)
C3—C8	1.398 (2)	C23—C28	1.389 (2)
C4—N2	1.379 (2)	C24—N22	1.396 (2)
C4—C5	1.389 (2)	C24—C25	1.389 (2)
C5—C6	1.383 (2)	C25—C26	1.382 (2)
C6—C7	1.404 (3)	C26—C27	1.406 (3)
C7—C8	1.377 (3)	C27—C28	1.376 (3)
O1—C1—C2	111.9 (1)	O21—C21—C22	112.4 (1)
C1—C2—N1	124.8 (1)	C21—C22—N21	121.8 (1)
C1—C2—N2	122.4 (1)	C21—C22—N22	125.1 (1)
N1—C2—N2	112.7 (1)	N21—C22—N22	113.2 (1)
N1—C3—C4	109.8 (1)	N21—C23—C24	105.4 (1)
N1—C3—C8	129.7 (1)	N21—C23—C28	132.0 (1)
C2—N1—C3	105.1 (1)	C22—N21—C23	107.3 (1)
C2—N2—C4	107.3 (1)	C22—N22—C24	105.0 (1)
C3—C4—N2	105.1 (1)	C23—C24—N22	109.1 (1)
C3—C4—C5	121.9 (1)	C23—C24—C25	120.0 (1)
C3—C8—C7	117.8 (2)	C23—C28—C27	116.8 (1)
N2—C4—C5	132.9 (1)	N22—C24—C25	130.8 (1)
C4—C3—C8	120.5 (1)	C24—C23—C28	122.5 (1)
C4—C5—C6	116.9 (2)	C24—C25—C26	117.8 (2)
C5—C6—C7	121.7 (2)	C25—C26—C27	121.4 (2)
C6—C7—C8	121.1 (2)	C26—C27—C28	121.4 (2)
O1—C1—C2—N1	98.63	O21—C21—C22—N21	27.78
O1—C1—C2—N2	−78.14	O21—C21—C22—N22	−152.28

Program used to solve structure: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Molecular drawing: *ORTEP* (Johnson, 1965). Full-matrix least-squares refinement: *SHELX* (Sheldrick, 1976). Following recommendations by Taylor & Kennard (1983), the H(N) atoms were placed at 1.03 Å from the parent N atom in the direction obtained from the refinement.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Isomeric Sulfites of 10β-Pinane-2,3α-diol

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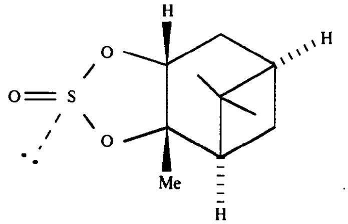
Abstract

In the title compounds, *cis*- and *trans*-3a,8,8-trimethyl-3a,4,5,6,7,7a-hexahydro-4,6-methano-1,3,2-dioxathiolane 2-oxide, $C_{10}H_{16}O_3S$, the five-membered ring adopts a half-chair (envelope) conformation. The orientation of the methyl group C7 substituted on C1, being either *cis* or *trans* to the exocyclic S=O bond, is the main structural difference between the two isomers.

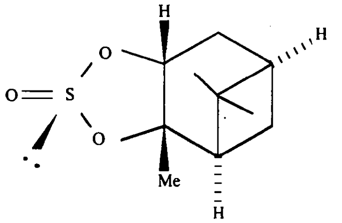
Comment

The structure determination of isomer (1) and isomer (2) of the cyclic sulfites of (±)-10β-pinane-

2,3α-diol was undertaken during the course of a study of a number of substituted 1,3,2-dioxathiolane 2-oxides (ethylene sulfites). The structure of isomer (1) has been previously reported (Brice, Coxon, Dansted, Hartshorn & Robinson, 1969) but with an *R* factor of 0.18.



(1)



(2)

Single crystals of (1) (m.p. 325 K) and (2) (m.p. 376 K) were obtained by cyclization of the pinanediol with thionyl chloride, followed by separation *via* HPLC and recrystallization from petroleum spirit (313–333 K). *PLUTON* (Spek, 1993) drawings of the two compounds are shown in Figs. 1 and 2. The X-ray structures show that (1) has the C7 methyl group *cis* to the exocyclic S=O bond and (2) is the *trans* isomer. Comparison of data for the two sulfites highlights distinct differences in S=O and S—O bond distances. Apart from minor variation in the ring angles, the greatest difference is between the torsion angle around the C1—C3 bond with −3.44 (74)° for (1) and 21.09 (67)° for (2). This may be compared with a typical value of 35° for a simple five-membered ring sulfite. Both sulfites contain the bicyclo[3.1.1]heptane ring system with very similar geometry. Finally, the absolute structures of the two sulfites were established and confirmed according to the procedure of Flack (1983).

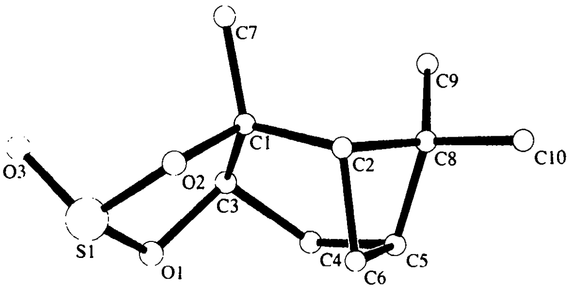


Fig. 1. View of (1) showing the atom-numbering scheme.

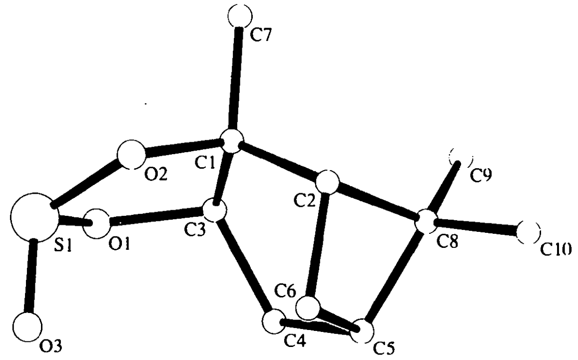


Fig. 2. View of (2) showing the atom-numbering scheme.

Experimental

Compound (1)

Crystal data

$C_{10}H_{16}O_3S$
M_r = 216.29
Orthorhombic
$P2_12_12_1$
a = 6.7060 (10) Å
b = 12.490 (2) Å
c = 12.965 (3) Å
V = 1085.9 (3) Å^3
Z = 4
D_x = 1.323 Mg m^{-3}
D_m = 1.4 Mg m^{-3}
D_m measured by flotation

Cu $K\alpha$ radiation
λ = 1.54180 Å
Cell parameters from 25 reflections
θ = 11–13°
μ = 2.502 mm^{-1}
T = 293 (2) K
Rhombic
0.38 × 0.36 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical
$T_{\min}$ = 0.980, $T_{\max}$ = 0.990
980 measured reflections
962 independent reflections
421 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.0112
$\theta_{\max}$ = 59.91°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0457
$wR(F^2)$ = 0.0869
S = 1.216
962 reflections
139 parameters
H atoms: calculated using *AFIX* in *SHELXL92* (Sheldrick, 1992)
$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = −0.018

$\Delta\rho_{\max}$ = 0.179 e Å^{-3}
$\Delta\rho_{\min}$ = −0.180 e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0114 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1	0.1096 (4)	0.0340 (2)	1.0110 (2)	0.0814 (9)
O1	0.1425 (9)	0.1563 (4)	1.0418 (4)	0.082 (2)
O2	−0.0144 (8)	0.0096 (4)	1.1125 (4)	0.069 (2)
O3	−0.0239 (9)	0.0295 (5)	0.9233 (4)	0.107 (2)
C1	−0.1278 (11)	0.1020 (6)	1.1523 (5)	0.050 (2)
C2	−0.0954 (12)	0.1025 (6)	1.2673 (5)	0.061 (2)
C3	−0.0261 (12)	0.2001 (6)	1.1007 (6)	0.060 (2)
C4	0.0634 (12)	0.2836 (6)	1.1741 (6)	0.069 (2)
C5	0.0621 (12)	0.2467 (7)	1.2872 (6)	0.061 (2)
C6	0.1286 (14)	0.1294 (6)	1.2890 (6)	0.072 (2)
C7	−0.3420 (11)	0.0857 (5)	1.1197 (5)	0.085 (3)
C8	−0.1482 (13)	0.2132 (5)	1.3205 (5)	0.058 (2)
C9	−0.3224 (13)	0.2809 (7)	1.2846 (6)	0.089 (3)
C10	−0.1636 (13)	0.1998 (6)	1.4380 (5)	0.096 (3)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

S1—O3	1.449 (6)	C2—C6	1.565 (10)
S1—O2	1.586 (5)	C2—C8	1.585 (9)
S1—O1	1.594 (5)	C3—C4	1.534 (9)
O1—C3	1.470 (8)	C4—C5	1.537 (9)
O2—C1	1.475 (7)	C5—C6	1.531 (9)
C1—C2	1.507 (8)	C5—C8	1.533 (9)
C1—C7	1.511 (9)	C8—C9	1.516 (9)
C1—C3	1.554 (9)	C8—C10	1.535 (9)
O3—S1—O2	108.7 (3)	O1—C3—C4	105.9 (6)
O3—S1—O1	108.6 (3)	O1—C3—C1	105.5 (6)
O2—S1—O1	92.8 (3)	C4—C3—C1	116.2 (6)
C3—O1—S1	112.4 (5)	C3—C4—C5	112.7 (6)
C1—O2—S1	114.2 (4)	C6—C5—C8	90.2 (6)
O2—C1—C2	106.0 (6)	C6—C5—C4	107.5 (7)
O2—C1—C7	106.7 (6)	C8—C5—C4	110.9 (6)
C2—C1—C7	114.5 (6)	C5—C6—C2	85.6 (6)
O2—C1—C3	103.9 (5)	C9—C8—C10	108.3 (7)
C2—C1—C3	111.0 (7)	C9—C8—C5	118.0 (6)
C7—C1—C3	113.8 (6)	C10—C8—C5	111.8 (6)
C1—C2—C6	108.5 (6)	C9—C8—C2	121.6 (6)
C1—C2—C8	113.8 (6)	C10—C8—C2	110.6 (6)
C6—C2—C8	87.1 (6)	C5—C8—C2	84.8 (6)

Compound (2)

Crystal data

$C_{10}H_{16}O_3S$
$M_r = 216.29$
Orthorhombic
$P2_12_12_1$
$a = 7.1760$ (10) Å
$b = 11.969$ (2) Å
$c = 12.621$ (2) Å
$V = 1084.0$ (3) Å^3
$Z = 4$
$D_x = 1.325$ Mg m^{-3}
$D_m = 1.4$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11\text{–}13°$
$\mu = 0.278$ mm^{-1}
$T = 293$ (2) K
Rhombic
0.38 × 0.35 × 0.30 mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical
$T_{min} = 0.987$, $T_{max} = 0.998$
935 measured reflections
897 independent reflections
531 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0136$
$\theta_{max} = 22.97°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -2 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0477$
$wR(F^2) = 0.1046$
$S = 1.182$
897 reflections
138 parameters
H atoms: calculated using *AFIX* in *SHELXL*92 (Sheldrick, 1992)

$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.008$
$\Delta\rho_{max} = 0.248$ e Å^{-3}
$\Delta\rho_{min} = -0.256$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1	−0.0198 (3)	0.0325 (2)	0.01537 (15)	0.0542 (6)
O1	0.0608 (6)	0.1581 (4)	0.0134 (4)	0.0553 (15)
O2	0.0794 (6)	−0.0027 (4)	−0.0944 (4)	0.0504 (14)
O3	−0.2179 (7)	0.0353 (5)	−0.0021 (4)	0.074 (2)
C1	0.1766 (9)	0.0891 (6)	−0.1517 (5)	0.038 (2)
C2	0.1073 (9)	0.0882 (5)	−0.2654 (5)	0.038 (2)
C3	0.1199 (11)	0.1962 (6)	−0.0913 (5)	0.043 (2)
C4	−0.0237 (11)	0.2698 (6)	−0.1462 (5)	0.055 (2)
C5	−0.0578 (9)	0.2359 (6)	−0.2608 (6)	0.045 (2)
C6	−0.1047 (10)	0.1110 (6)	−0.2648 (6)	0.049 (2)
C7	0.3830 (10)	0.0619 (7)	−0.1418 (6)	0.067 (3)
C8	0.1265 (11)	0.2066 (6)	−0.3187 (5)	0.047 (2)
C9	0.2974 (11)	0.2801 (6)	−0.3010 (6)	0.059 (2)
C10	0.1021 (13)	0.1979 (7)	−0.4388 (5)	0.065 (3)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

S1—O3	1.439 (5)	C2—C6	1.545 (9)
S1—O1	1.612 (5)	C2—C8	1.574 (9)
S1—O2	1.614 (5)	C3—C4	1.523 (9)
O1—C3	1.460 (8)	C4—C5	1.522 (9)
O2—C1	1.489 (7)	C5—C6	1.534 (10)
C1—C2	1.518 (8)	C5—C8	1.551 (10)
C1—C7	1.522 (9)	C8—C9	1.526 (10)
C1—C3	1.546 (9)	C8—C10	1.530 (9)
O3—S1—O1	109.3 (3)	C1—C2—C6	108.5 (6)
O3—S1—O2	108.1 (3)	C1—C2—C8	111.6 (5)
O1—S1—O2	94.1 (3)	C6—C2—C8	85.9 (6)
C3—O1—S1	114.2 (4)	O1—C3—C4	113.3 (6)
C1—O2—S1	115.6 (4)	O1—C3—C1	105.3 (5)
O2—C1—C2	107.5 (5)	C4—C3—C1	115.7 (5)
O2—C1—C7	104.9 (5)	C5—C4—C3	112.8 (6)
C2—C1—C7	113.3 (6)	C4—C5—C6	109.1 (6)
O2—C1—C3	104.4 (5)	C4—C5—C8	111.8 (6)
C2—C1—C3	112.7 (6)	C6—C5—C8	87.2 (6)
C7—C1—C3	113.1 (6)	C5—C6—C2	87.5 (5)

The structures were solved using *SHELXS*86 (Sheldrick, 1990), refinement was carried out using *SHELXL*93 (Sheldrick, 1993) and molecular graphics were prepared using *PLUTON*

(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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Acta Cryst. (1995). C**51**, 119–121

7*β*,8*β*-Epoxyfriedelane

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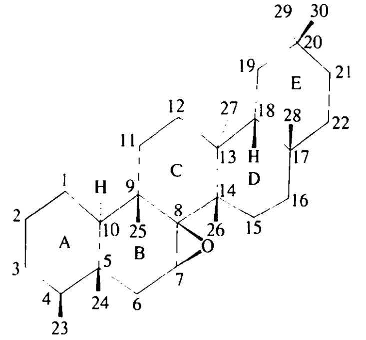
Abstract

The title compound, $C_{30}H_{50}O$, was produced by a series of chemical reactions from the parent compound putranjivadione 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 indentical 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 putranjivadione, 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 a chemical reactions from the parent compound putranjivadione. 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, Saski & Suzuki, 1964).



(I)

Several natural products possess the 2,3-epoxy-4-quinol structure (Closse, Mauli & Sigg, 1966; Brodasky, Stroman, Dietz & Mizsak, 1983; Box, Gilpin, Gwynn, Hanscomb, Spear & Brown, 1983; Read & Vining, 1963; Marumo, Saski & Suzuki, 1964). Mycochrysone, a metabolite discomycete, and cervicarcin, both antitumor agents produced by *Streptomyces ogaensis*, are typical examples (Read & Vining, 1963; Marumo, Saski & 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

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