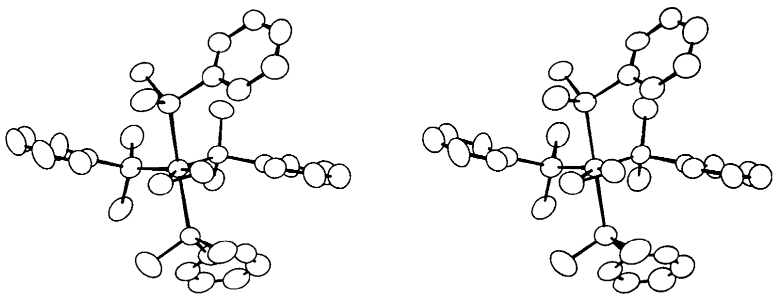

Fig. 2. Stereoscopic view of the cation $[IrO_2\{P(CH_3)_2C_6H_5\}_4]^+$.

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Crystal and Molecular Structure of the *p*-Bromobenzenesulphonate Derivative of the Complex Tetranortriterpenoid Prieurianin, $C_{44}H_{53}O_{18}SBr$

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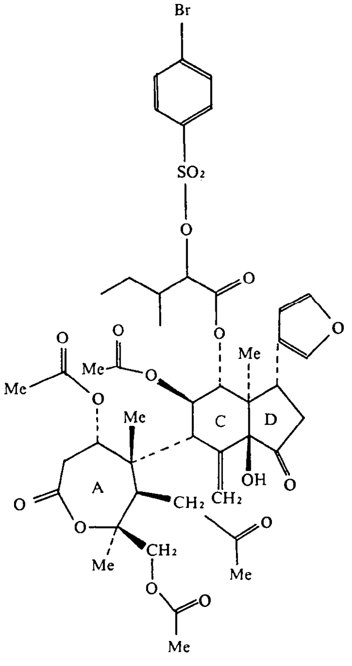
The structure of the title compound has been determined from 1926 independent reflexions collected on a diffractometer. The crystals are orthorhombic, space group $P2_12_12_1$, with $Z=4$, $a=11{\cdot}339$, $b=16{\cdot}371$, $c=27{\cdot}737$ Å. The structure was solved by a combination of the heavy-atom and direct-phasing techniques, and has been refined by least squares to a final R of 0·096.

Introduction

Prieurianin, a complex tetranortriterpenoid, was first isolated in 1965 by light petroleum extraction of the timber of *Trichilia prieuriana* (Meliaceae) (Bevan, Ekong & Taylor, 1965). However, until recently the structure has remained obscure since conventional spectroscopic studies, although indicating the presence of several of the functional groups, gave little information about the overall chemical constitution. Accordingly, we undertook an X-ray analysis of the *p*-bromobenzenesulphonate derivative of prieurianin (I) concurrently with a thorough spectroscopic analysis, which included ^{13}C NMR studies at elevated temperature with the more advanced techniques of proton-noise and continuous-wave decoupling, and ^1H NMR studies at a range of elevated and sub-ambient temperatures. Both the spectroscopic and crystallographic approaches independently led to correct elucidations of the molecular structure, and in addition the latter study also resolved several stereochemical ambiguities which remained from the spectroscopic studies (Gullo *et al.*, 1975). We describe here the details of the X-ray analysis; full accounts of the spectroscopic and chemical studies will be published elsewhere.



(I)

Experimental

Crystal data

Prieurianin p-bromobenzenesulphonate (solvated). $C_{44}H_{53}O_{18}SBr.(CH_2Cl_2)_{3/4}$, $M=981{\cdot}8$ (excluding solvent). Orthorhombic, $a=11{\cdot}339$, $b=16{\cdot}371$, $c=27{\cdot}737$ Å, $U=4963{\cdot}2$ Å^3, $D_m=1{\cdot}36$ g cm^{-3}, $Z=4$, $D_c=1{\cdot}31$ g cm^{-3} (excluding solvent), $F(000)=2174$. Space group $P2_12_12_1$. Mo $K\alpha$ radiation, $\lambda=0{\cdot}7107$ Å, μ(Mo K) $=10{\cdot}2$ cm^{-1}.

Crystallographic measurements

The cell parameters, initially determined photographically, were refined by least squares prior to the diffractometer data collections. Two sets of intensities were measured. Initially, a small crystal was exposed to Ni-filtered Cu $K\alpha$ radiation on a Hilger and Watts Y290 diffractometer, and with the $2\theta,\omega$-scan technique in the range 2θ $0 \rightarrow 114°$, the intensities of 3036 independent reflexions $[I>2\sigma_I,\ \sigma_I=\sqrt{(I+B_1+B_2)}]$ were measured. This set of data proved sufficient to allow solution (with difficulty) of the structure, but did not permit satisfactory refinement. This effect was eventually traced to an electronic fault in the counting chain of the diffractometer, which had produced random and otherwise undetectable errors in the intensity measurements. Accordingly, the same crystal was exposed to graphite-monochromated Mo radiation, and with the same data-collecting technique in the range 2θ $0 \rightarrow 50°$, the intensities of 1926 independent reflexions $(I>3\sigma_I)$ were remeasured. The structure was refined from the latter set of data. All intensities were corrected with Lorentz and polarization factors, but not for absorption.

Structure determination

The structure of prieurianin was solved from the initial set of diffraction data. Many of the difficulties experienced probably resulted directly from unsuspected failings in the data. Attempts to solve the structure by the heavy-atom technique met with only limited success. Inspection of a sharpened Patterson function yielded a convincing Br position, but no S position, and subsequent structure factor and electron density calculations rapidly ceased to yield improved structural information. Accordingly, attempts were made to solve the structure by direct-phasing techniques. With a starting set of five reflexions chosen to give rapid phase expansion, phases were calculated and refined by reiteration by the tangent-formula procedure with 432 reflexions of $|E|\geq 1{\cdot}35$. A subsequent E map indicated the presence of the heavy atom in the same location as that indicated by the Patterson function, and also indicated some skeletal fragments although the resolution was poor.

Concurrently with the above approach, a tangent-formula refinement of the phases appropriate to the heavy-atom position was carried out, in which a starting set of 280 reflexions ($|E|\geq 1{\cdot}50$) was used to derive the phases for 381 reflexions with $|E|\geq 1{\cdot}40$. The resulting E map agreed closely with that obtained above, showing fewer peaks, but with only slightly improved resolution. However, comparison of the two E maps allowed the selection of a number of atomic sites, which were used to initiate several cycles of structure factor and electron density calculations culminating in the eventual solution of the complete structure.

Structure refinement

Refinement of the structure by least squares converged when R was 0·096 and R^1 $(=\sum w\Delta^2/\sum w|F_o|^2)$ was 0·015. Details of the refinement are given in Table 1. It was at this stage of the analysis that the shortcomings of the original intensities were fully realized. An immediate improvement was obtained on substituting the new set of data, which additionally allowed identification of a molecule of methylene chloride

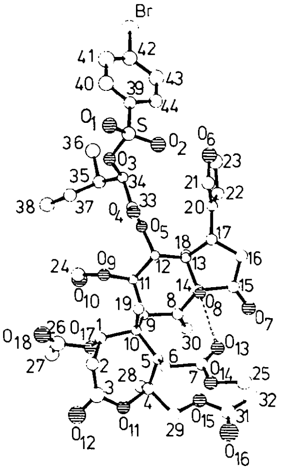


Fig. 1. A view of one molecule with the internal hydrogen bond shown by the broken line.

Table 1. *Course of refinement*

Cycles	Parameters refined	Final R	Final R'
1	x,y,z,U_{ov}, scale factor. Unit weights	0·276	0·075
2– 5	x,y,z,U_{iso}, scale factor. Unit weights	0·195	0·039
6– 7	x,y,z,U_{iso} (U_{ij} for Br), scale factor. Unit weights	0·178	0·034
8–12	x,y,z,U_{iso} (U_{ij} for Br), scale factor. Unit weights. New data set, with Mo $K\alpha$ radiation	0·125	0·022
13–17	x,y,z,U_{iso} (U_{ij} for Br), scale factor. Unit weights. Solvent molecule included and refined with overall population parameter	0·108	0·013
18–19	x,y,z,U_{iso} (U_{ij} for Br), scale factor. Unit weights. Solvent molecule included. Coordinates inverted to give correct enantiomorph	0·098	0·011
20–23	x,y,z,U_{iso} (U_{ij} for Br), scale factor. Weighting scheme applied. Solvent molecule included	0·096	0·012

partially present in the structure. This was included in the refinement with adjustment of an overall fractional population parameter, the final value of which was 0·74. In the final cycles of refinement, a weighting scheme of the form:

$$w=[A+B|F_o|+C|F_o|^2]^{-1}$$

was applied with coefficients $A=8{\cdot}349$, $B=0{\cdot}4737$, $C=0{\cdot}0013$.

Fractional coordinates and thermal parameters are listed in Table 2, while Table 3 contains molecular dimensions and pertinent non-bonded contacts. Estimated standard deviations quoted in Tables 2 and 3 are derived from the least-squares calculations, and should be regarded as minimum values. Details of some least-squares planes through various portions of the molecular framework are given in Table 4. Fig. 1 shows a view of one molecule and the atomic numbering.*

Table 2. *Fractional coordinates and isotropic thermal parameters* (Å^2)

	x	y	z	U_{iso}
Br	0·5559 (3)	0·1624 (2)	0·3891 (1)	–
S	0·4787 (5)	0·3368 (4)	0·6000 (2)	0·068 (2)
O(1)	0·5106 (16)	0·2830 (10)	0·6401 (6)	0·085 (5)
O(2)	0·3717 (16)	0·3785 (11)	0·5995 (11)	0·089 (5)
O(3)	0·5839 (12)	0·4018 (8)	0·6000 (5)	0·055 (4)
O(4)	0·4963 (13)	0·5328 (9)	0·6484 (5)	0·065 (4)
O(5)	0·5397 (11)	0·6163 (7)	0·5830 (4)	0·046 (3)
O(6)	0·2536 (17)	0·4778 (11)	0·5156 (7)	0·091 (5)
O(7)	0·2092 (14)	0·8982 (10)	0·5671 (6)	0·072 (5)
O(8)	0·3132 (11)	0·7879 (8)	0·6501 (4)	0·044 (3)
O(9)	0·6827 (12)	0·7017 (8)	0·6478 (5)	0·050 (4)
O(10)	0·8343 (16)	0·7377 (11)	0·5948 (7)	0·086 (5)
O(11)	0·6494 (14)	1·0265 (9)	0·7501 (5)	0·063 (4)
O(12)	0·8017 (20)	1·0014 (13)	0·7993 (8)	0·113 (7)
O(13)	0·2468 (14)	0·9190 (9)	0·7085 (6)	0·064 (4)
O(14)	0·2408 (15)	0·9680 (9)	0·7861 (6)	0·068 (4)
O(15)	0·4082 (14)	1·0817 (9)	0·6736 (6)	0·068 (4)
O(16)	0·2825 (21)	1·1574 (14)	0·7158 (9)	0·127 (8)
O(17)	0·7816 (13)	0·8833 (8)	0·6844 (5)	0·058 (4)
O(18)	0·9292 (19)	0·8087 (12)	0·7189 (7)	0·106 (6)
C(1)	0·6984 (17)	0·8411 (12)	0·7190 (7)	0·045 (5)
C(2)	0·7101 (21)	0·8803 (14)	0·7716 (8)	0·060 (6)
C(3)	0·7193 (27)	0·9714 (18)	0·7740 (10)	0·083 (8)
C(4)	0·5706 (19)	1·0092 (12)	0·7082 (8)	0·050 (5)
C(5)	0·5013 (17)	0·9277 (12)	0·7084 (7)	0·045 (5)
C(6)	0·4295 (17)	0·9230 (12)	0·7584 (7)	0·043 (5)
C(7)	0·2944 (19)	0·9350 (13)	0·7464 (8)	0·051 (6)
C(8)	0·4634 (17)	0·8649 (11)	0·6050 (7)	0·044 (5)
C(9)	0·5738 (16)	0·8364 (11)	0·6372 (6)	0·034 (4)
C(10)	0·5680 (17)	0·8442 (11)	0·6971 (6)	0·037 (5)
C(11)	0·5995 (15)	0·7447 (10)	0·6157 (6)	0·033 (4)
C(12)	0·4932 (15)	0·6871 (10)	0·6098 (6)	0·031 (4)
C(13)	0·4010 (16)	0·7262 (11)	0·5756 (7)	0·035 (5)
C(14)	0·3619 (17)	0·8074 (11)	0·6025 (7)	0·043 (5)
C(15)	0·2440 (20)	0·8283 (14)	0·5732 (8)	0·058 (6)
C(16)	0·1929 (20)	0·7508 (14)	0·5578 (8)	0·057 (6)
C(17)	0·2794 (18)	0·6844 (12)	0·5747 (7)	0·051 (5)
C(18)	0·4457 (18)	0·7481 (11)	0·5239 (6)	0·040 (5)
C(19)	0·5128 (17)	0·7710 (11)	0·7210 (7)	0·042 (5)
C(20)	0·2750 (19)	0·6100 (12)	0·5389 (7)	0·049 (5)
C(21)	0·2511 (23)	0·5324 (15)	0·5548 (9)	0·067 (7)
C(22)	0·2882 (20)	0·6063 (14)	0·4862 (8)	0·060 (6)
C(23)	0·2736 (27)	0·5227 (18)	0·4739 (10)	0·090 (9)
C(24)	0·8012 (22)	0·6998 (16)	0·6320 (9)	0·072 (7)
C(25)	0·1107 (26)	0·9815 (17)	0·7800 (10)	0·086 (9)
C(26)	0·9030 (24)	0·8602 (16)	0·6884 (10)	0·080 (8)
C(27)	0·9731 (23)	0·9061 (15)	0·6519 (9)	0·077 (7)
C(28)	0·6424 (19)	1·0305 (13)	0·6595 (8)	0·053 (6)
C(29)	0·4844 (22)	1·0816 (14)	0·7176 (9)	0·070 (7)
C(30)	0·4744 (19)	0·9295 (13)	0·5750 (8)	0·054 (6)
C(31)	0·3036 (24)	1·1222 (16)	0·6768 (10)	0·076 (8)
C(32)	0·2389 (29)	1·1211 (19)	0·6283 (11)	0·107 (10)
C(33)	0·5362 (17)	0·5437 (11)	0·6057 (7)	0·045 (5)
C(34)	0·5745 (17)	0·4757 (11)	0·5711 (7)	0·044 (5)
C(35)	0·7004 (19)	0·4951 (14)	0·5457 (8)	0·060 (6)
C(36)	0·7291 (23)	0·4295 (16)	0·5086 (9)	0·081 (7)
C(37)	0·7910 (20)	0·4988 (14)	0·5862 (8)	0·062 (6)
C(38)	0·9145 (24)	0·5302 (16)	0·5651 (9)	0·083 (8)
C(39)	0·4977 (19)	0·2858 (13)	0·5421 (8)	0·056 (6)
C(40)	0·5743 (25)	0·2214 (17)	0·5405 (10)	0·087 (8)
C(41)	0·5920 (27)	0·1848 (19)	0·4918 (11)	0·101 (10)
C(42)	0·5304 (23)	0·2117 (16)	0·4515 (9)	0·075 (7)
C(43)	0·4429 (25)	0·2748 (17)	0·4540 (10)	0·087 (8)
C(44)	0·4255 (22)	0·3138 (15)	0·5018 (9)	0·074 (7)
C(45)	0·6460 (50)	0·8002 (33)	0·2313 (19)	0·144 (18)
Cl(1)	0·7305 (12)	0·7514 (8)	0·1936 (4)	0·127 (6)
Cl(2)	0·5597 (21)	0·8675 (12)	0·1936 (7)	0·216 (8)

Anisotropic thermal parameters (Å^2) for Br

U_{11}	0·080 (2)	U_{12}	−0·014 (2)
U_{22}	0·088 (2)	U_{13}	0·026 (2)
U_{33}	0·108 (3)	U_{23}	−0·044 (2)

Table 3. *Interatomic distances and angles*

(*a*) Bonded distances (Å)

C(1)—C(2)	1·55 (3)	C(8)—C(14)	1·49 (3)
C(1)—C(10)	1·59 (3)	C(8)—C(30)	1·33 (3)
C(1)—O(17)	1·49 (2)	C(11)–C(12)	1·54 (2)
C(2)—C(3)	1·50 (4)	C(11)–O(9)	1·46 (2)
C(3)—O(11)	1·36 (3)	C(12)–C(13)	1·55 (2)
C(3)—O(12)	1·25 (4)	C(12)–O(5)	1·46 (2)
C(4)—O(11)	1·46 (3)	C(13)–C(14)	1·58 (3)
C(4)—C(5)	1·55 (3)	C(13)–C(17)	1·54 (3)
C(4)—C(28)	1·57 (3)	C(13)–C(18)	1·52 (3)
C(4)—C(29)	1·56 (3)	C(14)–C(15)	1·59 (3)
C(5)—C(6)	1·57 (3)	C(14)–O(8)	1·42 (2)
C(5)—C(10)	1·59 (3)	C(15)–C(16)	1·45 (3)
C(6)—C(7)	1·58 (3)	C(15)–O(7)	1·22 (3)
C(7)—O(13)	1·18 (3)	C(16)–C(17)	1·53 (3)
C(7)—O(14)	1·34 (3)	C(17)–C(20)	1·55 (4)
O(14)–C(25)	1·50 (3)	C(20)–C(21)	1·37 (3)
C(10)–C(9)	1·61 (2)	C(20)–C(22)	1·42 (3)
C(10)–C(19)	1·49 (3)	C(22)–C(23)	1·42 (4)
C(9)—C(8)	1·59 (3)	C(21)–O(6)	1·38 (3)
C(9)—C(11)	1·63 (2)	C(23)–O(6)	1·36 (3)
O(9)—C(24)	1·41 (3)	C(35)–C(36)	1·50 (3)
O(10)–C(24)	1·23 (3)	C(35)–C(37)	1·49 (3)
O(17)–C(26)	1·43 (3)	C(37)–C(38)	1·60 (4)
O(18)–C(26)	1·21 (3)	S——O(3)	1·60 (1)
C(26)–C(27)	1·47 (4)	S——O(2)	1·39 (2)
C(29)–O(15)	1·46 (3)	S——O(1)	1·43 (2)
O(15)–C(31)	1·36 (3)	S——C(39)	1·77 (2)
O(16)–C(31)	1·22 (4)	C(39)–C(40)	1·37 (4)
C(31)–C(32)	1·49 (4)	C(40)–C(41)	1·45 (4)
O(5)—C(33)	1·33 (2)	C(41)–C(42)	1·36 (4)
O(4)—C(33)	1·24 (2)	C(42)–C(43)	1·43 (4)
C(33)–C(34)	1·51 (3)	C(43)–C(44)	1·44 (4)
C(34)–C(35)	1·61 (3)	C(44)–C(39)	1·43 (3)
C(34)–O(3)	1·44 (2)	Br——C(42)	1·88 (3)
C(45)–Cl(1)	1·60 (6)	C(45)–Cl(2)	1·79 (6)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31590 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3 (*cont.*)

(*b*) Interbond angles (°)

C(2)—C(1)—C(10)	113·6 (16)	C(5)—C(10)–C(1)	113·5 (15)	C(8)—C(14)–C(15)	122·5 (16)	C(29)–O(15)–C(31)	117·7 (18)
C(2)—C(1)—O(17)	108·4 (16)	C(5)—C(10)–C(9)	106·1 (14)	C(8)—C(14)–O(8)	113·6 (15)	O(15)–C(31)–C(32)	111·6 (22)
C(10)–C(1)—O(17)	110·3 (13)	C(5)—C(10)–C(19)	114·1 (15)	C(15)–C(14)–O(8)	99·4 (15)	O(15)–C(31)–O(16)	117·2 (24)
C(1)—C(2)—C(3)	117·2 (19)	C(1)—C(10)–C(9)	109·0 (14)	C(14)–C(15)–C(16)	106·7 (17)	O(16)–C(31)–C(32)	131·0 (27)
C(2)—C(3)—O(11)	126·9 (20)	C(1)—C(10)–C(19)	101·9 (14)	C(14)–C(15)–O(7)	122·7 (19)	C(12)–O(5)—C(33)	118·1 (13)
C(2)—C(3)—O(12)	117·7 (25)	C(9)—C(10)–C(19)	112·3 (14)	C(16)–C(15)–O(7)	130·6 (21)	O(5)—C(33)–C(34)	111·6 (16)
O(11)–C(3)—O(12)	115·4 (25)	C(10)–C(9)—C(8)	118·9 (14)	C(15)–C(16)–C(17)	106·3 (18)	O(5)—C(33)–O(4)	124·0 (17)
C(3)—O(11)–C(4)	126·1 (18)	C(10)–C(9)—C(11)	115·5 (13)	C(16)–C(17)–C(13)	105·3 (16)	O(4)—C(33)–C(34)	124·1 (16)
O(11)–C(4)—C(5)	118·3 (16)	C(8)—C(9)—C(11)	102·7 (13)	C(16)–C(17)–C(20)	110·8 (17)	C(33)–C(34)–C(35)	111·6 (16)
O(11)–C(4)—C(28)	106·0 (16)	C(9)—C(8)—C(14)	116·6 (15)	C(13)–C(17)–C(20)	112·8 (16)	C(33)–C(34)–O(3)	108·2 (14)
O(11)–C(4)—C(29)	96·5 (15)	C(9)—C(8)—C(30)	119·1 (17)	C(17)–C(20)–C(21)	123·0 (18)	C(35)–C(34)–O(3)	109·1 (15)
C(5)—C(4)—C(28)	117·2 (16)	C(14)–C(8)—C(30)	123·1 (18)	C(17)–C(20)–C(22)	130·1 (19)	C(34)–C(35)–C(36)	109·4 (18)
C(5)—C(4)—C(29)	109·7 (17)	C(9)—C(11)–C(12)	117·4 (14)	C(21)–C(20)–C(22)	106·9 (19)	C(34)–C(35)–C(37)	108·1 (17)
C(28)–C(4)—C(29)	106·9 (16)	C(9)—C(11)–O(9)	110·6 (13)	C(20)–C(22)–C(23)	105·0 (20)	C(36)–C(35)–C(37)	111·1 (19)
C(4)—C(5)—C(6)	108·0 (16)	C(12)–C(11)–O(9)	105·8 (13)	C(22)–C(23)–O(6)	110·7 (22)	C(35)–C(37)–C(38)	111·1 (18)
C(4)—C(5)—C(10)	119·9 (16)	C(11)–C(12)–C(13)	109·9 (13)	C(20)–C(21)–O(6)	111·2 (20)	C(34)–O(3)—S	120·3 (12)
C(6)—C(5)—C(10)	111·6 (15)	C(11)–C(12)–O(5)	104·7 (13)	C(21)–O(6)—C(23)	106·0 (20)	O(3)—S——O(2)	108·9 (9)
C(5)—C(6)—C(7)	108·9 (15)	C(13)–C(12)–O(5)	106·5 (13)	C(24)–O(9)—C(11)	116·8 (15)	O(3)—S——O(1)	102·8 (9)
C(6)—C(7)—O(13)	126·4 (19)	C(12)–C(13)–C(14)	105·8 (14)	O(9)–C(24)–O(10)	121·5 (22)	O(3)—S——C(39)	102·8 (9)
C(6)—C(7)—O(14)	109·3 (17)	C(12)–C(13)–C(17)	115·9 (15)	C(39)–S——O(2)	109·1 (11)	C(42)–C(43)–C(44)	117·0 (23)
O(13)–C(7)—O(14)	124·3 (20)	C(12)–C(13)–C(18)	114·6 (15)	C(39)–S——O(1)	109·5 (10)	C(43)–C(44)–C(39)	116·7 (22)
C(7)—O(14)–C(25)	114·9 (18)	C(14)–C(13)–C(17)	97·5 (14)	O(1)—S——O(2)	122·0 (10)	C(44)–C(39)–C(40)	125·9 (22)
C(14)–C(13)–C(18)	108·1 (14)	C(26)–O(17)–C(1)	116·1 (16)	S——C(39)–C(40)	118·0 (18)	C(41)–C(42)–Br	119·1 (21)
C(17)–C(13)–C(18)	112·9 (15)	O(17)–C(26)–C(27)	109·6 (21)	S——C(39)–C(44)	116·0 (17)	C(43)–C(42)–Br	117·2 (18)
C(13)–C(14)–C(8)	109·7 (15)	O(17)–C(26)–O(18)	118·1 (23)	C(39)–C(40)–C(41)	115·9 (24)	Cl(1) –C(45)–Cl(2)	106·3 (29)
C(13)–C(14)–C(15)	101·2 (15)	O(18)–C(26)–C(27)	132·3 (26)	C(40)–C(41)–C(42)	120·5 (27)		
C(13)–C(14)–O(8)	109·2 (14)	C(4)—C(29)–O(15)	104·0 (17)	C(41)–C(42)–C(43)	123·7 (24)		

(*c*) Selected intramolecular non-bonded distances (Å)

C(1) · · · · O(9)	2·98	C(19) · · · O(8)	2·96	C(37) · · · O(3)	2·86
C(1) · · · · O(18)	2·67	C(19) · · · O(9)	2·97	C(40) · · · O(1)	2·94
C(2) · · · · O(18)	3·09	C(24) · · · C(26)	3·24	C(40) · · · O(3)	3·36
C(3) · · · · O(17)	2·88	C(24) · · · O(18)	3·27	C(44) · · · O(2)	2·88
C(5) · · · · O(13)	2·89	C(25) · · · O(13)	2·66	C(44) · · · O(3)	3·49
C(5) · · · · O(15)	2·89	C(26) · · · O(10)	3·30	C(44) · · · O(6)	3·34
C(6) · · · · C(19)	2·84	C(28) · · · C(30)	3·39	S · · · · · · O(4)	3·46
C(6) · · · · C(29)	2·88	C(28) · · · O(15)	2·81	O(2) · · · · O(4)	3·17
C(6) · · · · O(11)	3·02	C(28) · · · O(17)	2·95	O(2) · · · · O(6)	3·07
C(6) · · · · O(15)	3·35	C(29) · · · O(16)	2·61	O(3) · · · · O(4)	2·69
C(9) · · · · C(28)	3·33	C(30) · · · O(7)	3·06	O(5) · · · · O(9)	2·76
C(11) · · · O(10)	2·72	C(31) · · · O(13)	3·49	O(7) · · · · O(8)	3·10
C(12) · · · O(4)	2·73	C(34) · · · O(2)	2·90	O(8) · · · · O(13)	2·76
C(18) · · · C(30)	3·29	C(35) · · · O(5)	2·87	O(9) · · · · O(17)	3·32
C(18) · · · O(5)	2·88	C(36) · · · O(3)	2·98	O(13) · · · O(15)	3·36

(*d*) Selected intermolecular distances (Å)

O(1) · · · · O(15)$^{\mathrm{i}}$	3·61	O(11) · · · O(4)$^{\mathrm{iii}}$	3·18	Br · · · · · · O(2)$^{\mathrm{iv}}$	3·65
O(1) · · · · C(31)$^{\mathrm{i}}$	3·66	O(14) · · · C(10)$^{\mathrm{iii}}$	3·47	C(6) · · · · O(6)$^{\mathrm{iv}}$	3·24
C(27) · · · O(13)$^{\mathrm{ii}}$	3·46	O(16) · · · C(35)$^{\mathrm{iii}}$	3·42	C(8) · · · · O(7)$^{\mathrm{v}}$	3·49
C(27) · · · O(7)$^{\mathrm{ii}}$	3·51	C(32) · · · O(4)$^{\mathrm{iii}}$	3·36	C(9) · · · · O(7)$^{\mathrm{v}}$	3·48
O(12) · · · C(25)$^{\mathrm{ii}}$	3·56	C(36) · · · O(4)$^{\mathrm{iii}}$	3·18	O(10) · · · C(22)$^{\mathrm{v}}$	3·42
				O(1) · · · · Cl(1)$^{\mathrm{vi}}$	3·31

Roman numeral superscripts refer to the following equivalent positions relative to a molecule at (x,y,z):

(i)	x	$-1+y$	z	(ii)	$1+x$	y	z
(iii)	$1-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$	(iv)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
(v)	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$1-z$	(vi)	$\frac{3}{2}-x$	$1-y$	$\frac{1}{2}+z$

(*e*) Selected torsion angles (°)

C(40)–C(39)–S——O(1)	−23	C(17)–C(16)–C(15)–C(14)	−3
C(40)–C(39)–S——O(2)	−159	C(16)–C(15)–C(14)–C(13)	31
C(40)–C(39)–S——O(3)	86	C(16)–C(15)–C(14)–C(8)	153
C(39)–S——O(3)—C(34)	78	C(12)–C(13)–C(17)–C(20)	−83
S——O(3)—C(34)–C(35)	−140	C(13)–C(17)–C(20)–C(22)	−64
S——O(3)—C(34)–C(35)	98	C(8)—C(9)—C(10)–C(19)	87
O(3)—C(34)–C(35)–C(36)	65	C(1)—C(10)–C(5)—C(4)	36
O(3)—C(34)–C(35)–C(37)	−56	C(10)–C(5)—C(4)—O(11)	−74
C(34)–C(35)–C(37)–C(38)	−172	C(5)—C(4)—O(11)–C(3)	39
O(3)—C(34)–C(33)–O(5)	172	C(4)—O(11)–C(3)—C(2)	−16
C(34)–C(33)–O(5)—C(12)	174	O(11)–C(3)—C(2)—C(1)	48

Table 3 (*cont.*)

C(33)–O(5)—C(12)–C(13)	−125	C(3)—C(2)—C(1)—C(10)	−81
C(12)–C(13)–C(14)–C(8)	65	C(2)—C(1)—C(10)–C(5)	40
C(13)–C(14)–C(8)—C(9)	−64	C(3)—C(2)—C(1)—O(17)	42
C(14)–C(8)—C(9)—C(11)	50	C(2)—C(1)—O(17)–C(26)	78
C(30)–C(8)—C(9)—C(11)	−118	C(1)—O(17)–C(26)–C(27)	179
C(8)—C(9)—C(11)–C(12)	−47	C(19)–C(10)–C(5)—C(6)	25
C(9)—C(11)–C(12)–C(13)	57	C(10)–C(5)—C(6)—C(7)	−118
C(9)—C(11)–O(9)—C(24)	−99	C(5)—C(6)—C(7)—O(14)	−152
C(11)–O(9)—C(24)–O(10)	5	C(6)—C(7)—O(14)–C(25)	−179
C(11)–C(12)–C(13)–C(17)	−168	C(3)—O(11)–C(4)—C(29)	155
C(12)–C(13)–C(17)–C(16)	156	O(11)–C(4)—C(29)–O(15)	171
C(14)–C(13)–C(17)–C(16)	45	C(4)—C(29)–O(15)–C(31)	162
C(13)–C(17)–C(16)–C(15)	−27	C(29)–O(15)–C(31)–C(32)	177

Mean e.s.d. = 2°.

Table 4. *Least-squares planes*

(*a*) Equations of planes

X, Y, and Z are orthogonal coordinates in Å.

(i) $0{\cdot}7168X+0{\cdot}6627Y-0{\cdot}2166Z+3{\cdot}9696=0$

(ii) $0{\cdot}9818X-0{\cdot}1460Y+0{\cdot}1218Z+3{\cdot}3468=0$

(iii) $-0{\cdot}3939X+0{\cdot}5269Y+0{\cdot}7531Z+17{\cdot}5039=0$

(iv) $-0{\cdot}5115X-0{\cdot}0468Y+0{\cdot}8579Z+11{\cdot}0785=0$

(v) $0{\cdot}6038X-0{\cdot}0180Y+0{\cdot}7969Z-11{\cdot}8424=0$

(*b*) Deviations of atoms from planes (Å)

(i)	Br	0·06	S	0·10	O(1)	−0·46
	O(2)	−0·31	C(39)	0·04*	C(40)	−0·03*
	C(41)	−0·00*	C(42)	0·02*	C(43)	−0·02*
	C(44)	−0·01*				
(ii)	C(17)	0·00	C(20)	0·01*	C(21)	−0·02*
	C(22)	0·00*	C(23)	−0·01*	O(6)	0·01*
(iii)	C(8)	0·07*	C(9)	−0·02*	C(14)	−0·02*
	C(30)	−0·03*				
(iv)	C(13)	−0·78	C(17)	−0·06	C(14)	0·001*
	C(15)	−0·005*	C(16)	0·001*	O(7)	0·002*
(v)	C(1)	1·06	C(4)	0·36	C(5)	−0·09
	C(10)	0·63	C(2)	0·003*	C(3)	−0·011*
	O(11)	0·004*	O(12)	0·004*		

(*c*) Dihedral angles between planes

(i) and (ii) 54·5°, (ii) and (iv) 113·0°, (iii) and (iv) 34·7°

* Denotes atom used to define plane.

Discussion

In view of the limited accuracy of the present analysis, resulting from a set of data which is small in relation to the number of atomic parameters, we limit our discussion to a brief mention of the salient features of the solid-state conformation.

Prieurianin *p*-bromobenzenesulphonate is characterized by a single-bond linkage between the lactone section of the molecule and the *C* and *D* ring portion, allowing the possibility of rotation of the lactone group about this bond. However, such rotation is likely to be somewhat hindered both by steric interactions and by hydrogen bonding involving the C(14) *β*-hydroxyl group, evidence for the latter having been observed in the IR spectrum. The present analysis has revealed that this hydrogen bonding is intramolecular [O(8)···O(13) 2·76 Å]. However, the broadness of the solution NMR spectra at ambient temperatures indicates a range of environmental conditions in the molecule, which vanishes at elevated temperatures with a consequent sharpening of the spectra, presumably as the greater thermal motion produces a uniform time-averaged environment. Correspondingly, at reduced temperature the multiplicities of some peaks have been interpreted as showing the presence of several conformers differing in the rotation about C(9)–C(10) and/or the conformation of the lactone ring. Inspection of a model reveals that in addition to the observed hydrogen bonding, a rotation of *ca* 180° about C(9)–C(10) would place the C(1) acetyl group in a position suitable for hydrogen bonding with the C(14) hydroxyl function.

The conformation of the ε-lactone ring is best described as a boat, distorted by the presence of the planar lactone group and with C(2) and C(5) in apical positions. The chair conformation of ring *C* and the puckered conformation of ring *D* are both normal for triterpenoid systems, although in the present case the C(8) exocyclic methylene group and the C(15) carbonyl function must impart some additional restrictions.

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