1770 measured reflections
1443 independent reflections
930 observed reflections [$I \geq 2.0\sigma(I)$]
3 standard reflections
frequency: 60 min
intensity variation: 6%

Refinement

$R = 0.0478$
$wR = 0.0545$
$S = 1.22$
930 reflections
154 parameters
Isotropic H atom refined using [U = U(carrier atoms) + 0.02 Å^2]
$w = 1.0/[\sigma^2(F) + 0.002F^2]$
Extinction correction: none
$(\Delta/\sigma)_{max} = 0.487$ [C(2) U_{33}]
$\Delta\rho_{max} = 0.234$ e Å^{-3}
$\Delta\rho_{min} = -0.217$ e Å^{-3}
Atomic scattering factors from *SHELX*76

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

U_{eq} = 1/3(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
O(1)	0.5181 (7)	0.0983 (2)	0.3856 (7)	0.071 (2)
O(3)	0.4599 (5)	0.0603 (2)	0.0763 (7)	0.054 (2)
O(6)	0.0867 (6)	0.0610 (2)	−0.0054 (8)	0.073 (2)
O(16)	0.4184 (6)	0.3500 (2)	0.3925 (7)	0.060 (2)
N(8)	0.4305 (6)	0.1461 (2)	0.0959 (7)	0.043 (2)
C(2)	0.4743 (9)	0.1018 (2)	0.2053 (11)	0.050 (2)
C(4)	0.3869 (10)	0.0746 (3)	−0.1276 (10)	0.056 (2)
C(5)	0.2123 (10)	0.0462 (3)	−0.1627 (11)	0.062 (3)
C(7)	0.3621 (10)	0.1335 (2)	−0.1210 (10)	0.060 (3)
C(9)	0.4303 (8)	0.1975 (2)	0.1780 (9)	0.042 (2)
C(10)	0.5203 (8)	0.2099 (2)	0.3626 (9)	0.047 (2)
C(11)	0.5191 (8)	0.2605 (2)	0.4407 (8)	0.046 (2)
C(12)	0.4327 (8)	0.2993 (2)	0.3310 (9)	0.043 (2)
C(13)	0.3443 (9)	0.2877 (2)	0.1391 (10)	0.051 (3)
C(14)	0.3431 (8)	0.2372 (3)	0.0653 (9)	0.044 (2)
C(15)	−0.0908 (11)	0.0409 (3)	−0.0372 (15)	0.089 (3)
C(17)	0.4951 (11)	0.3643 (3)	0.5887 (11)	0.069 (3)

Table 4. *Geometric parameters* (Å, °) *for compound* (II)

O(1)—C(2)	1.187 (8)	N(8)—C(9)	1.417 (7)
O(3)—C(2)	1.345 (8)	C(4)—C(5)	1.484 (10)
O(3)—C(4)	1.442 (8)	C(4)—C(7)	1.522 (9)
O(6)—C(5)	1.404 (9)	C(9)—C(10)	1.376 (8)
O(6)—C(15)	1.408 (9)	C(9)—C(14)	1.396 (9)
O(16)—C(12)	1.361 (7)	C(11)—C(10)	1.389 (7)
O(16)—C(17)	1.409 (8)	C(12)—C(11)	1.367 (8)
N(8)—C(2)	1.368 (8)	C(13)—C(12)	1.406 (9)
N(8)—C(7)	1.494 (8)	C(14)—C(13)	1.377 (9)
C(2)—O(3)—C(4)	111.7 (5)	O(6)—C(5)—C(4)	108.7 (6)
C(5)—O(6)—C(15)	113.6 (6)	N(8)—C(7)—C(4)	101.5 (5)
C(12)—O(16)—C(17)	118.0 (5)	N(8)—C(9)—C(14)	119.5 (5)
C(2)—N(8)—C(7)	111.2 (5)	N(8)—C(9)—C(10)	121.7 (5)
C(2)—N(8)—C(9)	126.0 (5)	C(10)—C(9)—C(14)	118.8 (5)
C(7)—N(8)—C(9)	122.5 (5)	C(9)—C(10)—C(11)	121.0 (5)
O(1)—C(2)—O(3)	122.9 (5)	C(10)—C(11)—C(12)	120.2 (5)
O(1)—C(2)—N(8)	127.7 (6)	C(11)—C(12)—O(16)	125.9 (5)
O(3)—C(2)—N(8)	109.4 (6)	C(13)—C(12)—O(16)	114.4 (5)
O(3)—C(4)—C(5)	109.0 (6)	C(11)—C(12)—C(13)	119.7 (5)
O(3)—C(4)—C(7)	105.8 (5)	C(12)—C(13)—C(14)	119.6 (5)
C(5)—C(4)—C(7)	112.9 (6)	C(9)—C(14)—C(13)	120.7 (5)

The structures were solved with *SHELXS*86 (Sheldrick, 1985) and refined with *SHELX*76 (Sheldrick, 1976) by full-matrix least squares. The *XRAY*76 program (Stewart *et al.*, 1976) was used for geometry analysis. The *ORTEP* program (Johnson, 1965) was used to obtain the stereoscopic representations of the molecules and crystal packing.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71392 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1028]

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Structure of *cyclo*-(L-Threonyl-D-valyl-L-prolyl-sarcosyl-*N*-methyl-L-valyl-O_{Thr}) at 153 K

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Abstract

The crystal structure of *cyclo*-(L-Thr-D-Val-L-Pro-Sar-*N*-L-MeVal-O_{Thr}), $C_{23}H_{39}N_5O_6.HCl.MeOH.H_2O$ is reported. This cyclic pentapeptide lactone represents one

of the two peptide units of actinomycin and is a 16-membered depsipeptide. The backbone adopts a flat conformation similiar to that found for an analogous *N*-protected pentapeptide lactone by Mauger, Stuart, Ferretti & Silverton [*J. Am. Chem. Soc.* (1985), **107**, 7154-7163].

Comment

Actinomycins (Waksman & Woodruff, 1940; Brockmann, 1960) are naturally occurring, very toxic antibiotics with outstanding antibacterial and cytostatic properties. They consist of two pentapeptide lactone rings which are linked by a 2-amino-4,6-dimethyl-3-oxophenoxazine-1,9-dicarboxylic acid chromophore *via* amide bonds to the threonine residues. The chromophore intercalates between guanine/cytosine pairs of the DNA double helix thus inhibiting the DNA-dependent RNA synthesis. In solution, the single-peptide lactone ring can adopt two completely different conformations designated with *A* and *C* (Lackner, 1972). The *A* type (in acetone) is very similar to the conformation found in the actinomycin *D* molecule (Ginell, Lessinger & Berman, 1988) or in actinomycin/deoxyguanosine complexes (Jain & Sobell, 1972; Takusagawa, Dabrow, Neidle & Berman, 1982). It is characterized by two *cis* amide bonds Val–Pro and Pro–Sar and the absence of intra-annular hydrogen bonds. The *C* type (in moist chloroform) contains only *trans* amide bonds and is apparently stabilized by an intramolecular hydrogen bond $N—H_{Val}\cdots O{=}C_{Sar}$ (Lackner, 1975).

The crystal structure of one peptide molecule is shown in Fig. 1. All bond lengths and angles are within the normal range for small cyclic peptides (Hossain & van der Helm, 1978; Mauger, Stuart, Highet & Silverton, 1982; Karle, Gibson & Karle 1970; Karle, 1978, 1979, 1981). All peptide bonds are essentially planar, the Thr-Val and Sar-MeVal are *trans*, the Val-Pro and Pro-Sar are *cis*.

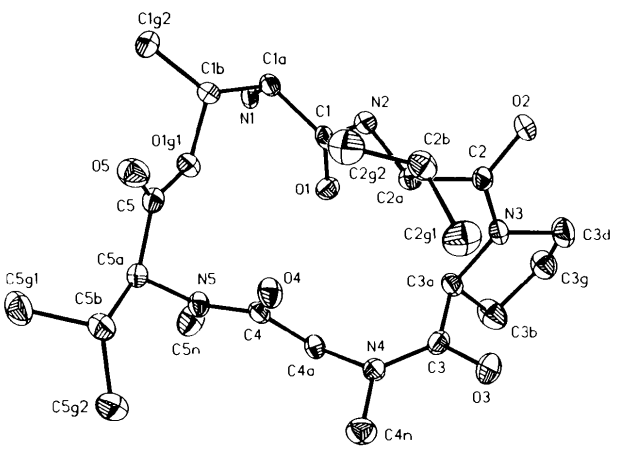

Fig. 1. Structure of the title compound showing 50% probability displacement ellipsoids. The H atoms and the solvent molecules are omitted for clarity.

The conformation of the present structure is very similar to that found in the *N*-protected peptide lactone with *N*-methyl-L-alanine instead of *N*-methyl-L-valine (Mauger, Stuart, Ferretti & Silverton, 1985). In both cases the *A* conformation is observed. The peptide crystallizes as the hydrochloride with one methanol molecule and one water molecule in the asymmetric unit. The extensive hydrogen bonding is shown in Fig. 2. Bond lengths and angles of all hydrogen bonds are summarized in Table 3. The dimensions of all hydrogen bonds are comparable with values given by Jeffrey & Saenger (1991). The water molecule is three-coordinated. The Cl^- ion is four-coordinated with one hydrogen bond to the minor component of the disordered methanol molecule. The strong hydrogen-bonding pattern is presumably essential for the crystallization of the pentapeptide.

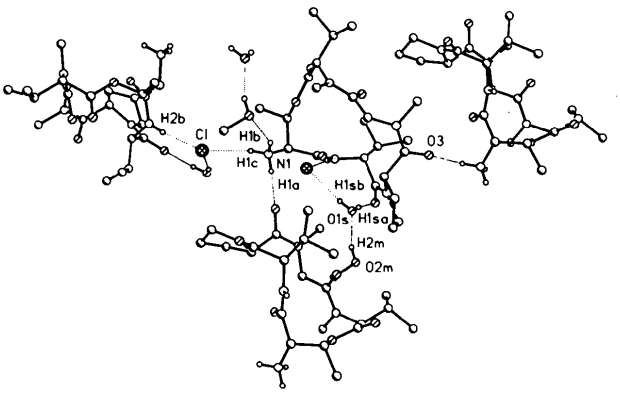

Fig. 2. Hydrogen-bonding pattern in the crystal.

Experimental

Crystal data

$C_{23}H_{39}N_5O_6.HCl.CH_3OH.H_2O$
M_r = 568.11
Orthorhombic
$P2_12_12_1$
a = 11.004 (3) Å
b = 13.482 (4) Å
c = 19.935 (2) Å
V = 2957.5 (12) Å^3
Z = 4
D_x = 1.276 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 56 reflections
θ = 10-12.5°
μ = 0.181 mm^{-1}
T = 153 (2) K
Plates
1.00 × 0.80 × 0.40 mm
Colourless

Data collection

Stoe Siemens four-circle diffractometer
Profile data from $2\theta/\omega$ scans
Absorption correction: none
7076 measured reflections
5195 independent reflections
4852 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0241
θ_{max} = 24.98°
h = −13 → 13
k = −16 → 16
l = −23 → 23
3 standard reflections
frequency: 90 min
intensity variation: none

Refinement

Refinement on F^2
$R[F > 4\sigma(F)] = 0.0334$
$wR(F^2) = 0.0892$
$S = 1.065$
5193 reflections
406 parameters
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.8536P]$
where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max} = 0.264$ e Å^{-3}
$\Delta\rho_{min} = -0.231$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.4)
Absolute configuration: Flack (1983)

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

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cl	0.86113 (5)	0.38978 (4)	0.51491 (3)	0.03771 (15)
O1*S*	0.1348 (2)	0.09497 (14)	0.58555 (9)	0.0419 (4)
O2*M*	−0.0290 (7)	0.2198 (5)	0.6446 (3)	0.0232 (12)
C2*M*	0.0060 (9)	0.3213 (7)	0.6404 (5)	0.030 (2)
O2*M*′	0.0298 (6)	0.3184 (6)	0.6277 (4)	0.0266 (15)
C2*M*′	−0.0228 (13)	0.2213 (8)	0.6279 (6)	0.025 (2)
C1	0.5845 (2)	0.10385 (14)	0.64123 (10)	0.0195 (4)
O1	0.63537 (12)	0.10834 (10)	0.69555 (6)	0.0241 (3)
N1	0.7230 (2)	0.23305 (12)	0.60434 (9)	0.0226 (4)
C1*A*	0.6391 (2)	0.15466 (14)	0.57998 (10)	0.0214 (4)
C1*B*	0.7073 (2)	0.07790 (15)	0.53787 (10)	0.0230 (4)
O1*G*1	0.79494 (12)	0.03554 (10)	0.58398 (7)	0.0231 (3)
C1*G*2	0.7713 (2)	0.1204 (2)	0.47687 (11)	0.0343 (5)
C2	0.3469 (2)	0.02095 (14)	0.72347 (10)	0.0206 (4)
O2	0.24634 (12)	0.04766 (11)	0.70199 (7)	0.0270 (3)
N2	0.48410 (14)	0.05128 (12)	0.62850 (8)	0.0207 (3)
C2*A*	0.4395 (2)	−0.02421 (14)	0.67490 (10)	0.0203 (4)
C2*B*	0.3773 (2)	−0.10925 (14)	0.63630 (10)	0.0259 (4)
C2*G*1	0.3526 (2)	−0.1946 (2)	0.68483 (13)	0.0379 (5)
C2*G*2	0.4521 (2)	−0.1454 (2)	0.57702 (11)	0.0342 (5)
C3	0.5267 (2)	−0.09341 (14)	0.82455 (9)	0.0218 (4)
O3	0.44953 (13)	−0.15274 (11)	0.84434 (8)	0.0356 (4)
N3	0.37391 (15)	0.02887 (12)	0.78820 (8)	0.0240 (4)
C3*A*	0.4946 (2)	0.01583 (14)	0.81899 (10)	0.0222 (4)
C3*B*	0.4778 (2)	0.0597 (2)	0.89015 (12)	0.0378 (5)
C3*G*	0.3643 (3)	0.1204 (4)	0.8863 (2)	0.0341 (13)
C3*D*	0.2860 (2)	0.0711 (2)	0.83619 (11)	0.0332 (5)
C3*G*′	0.3492 (5)	0.0654 (10)	0.9026 (3)	0.034 (3)
C4	0.7737 (2)	−0.09325 (13)	0.71500 (9)	0.0190 (4)
O4	0.70556 (12)	−0.14303 (10)	0.68008 (7)	0.0254 (3)
C4*A*	0.7406 (2)	−0.06619 (14)	0.78726 (10)	0.0209 (4)
N4	0.63886 (14)	−0.12558 (11)	0.81047 (8)	0.0208 (3)
C4*N*	0.6636 (2)	−0.23183 (14)	0.81806 (11)	0.0294 (5)
C5	0.8306 (2)	−0.05866 (14)	0.57239 (10)	0.0226 (4)
O5	0.79912 (14)	−0.10574 (11)	0.52464 (7)	0.0318 (3)
N5	0.88197 (14)	−0.06071 (12)	0.69293 (8)	0.0210 (3)
C5*A*	0.9216 (2)	−0.09074 (14)	0.62587 (10)	0.0223 (4)
C5*B*	0.9553 (2)	−0.20151 (15)	0.61866 (11)	0.0279 (4)
C5*G*1	1.0487 (2)	−0.2118 (2)	0.56275 (11)	0.0340 (5)
C5*G*2	1.0030 (3)	−0.2448 (2)	0.68326 (13)	0.0461 (6)
C5*N*	0.9585 (2)	0.0060 (2)	0.73164 (11)	0.0340 (5)

Table 2. *Geometric parameters* (Å, °)

C1—O1	1.220 (2)	C3—O3	1.232 (2)
C1—N2	1.337 (2)	C3—N4	1.338 (3)
C1—C1*A*	1.523 (3)	C3—C3*A*	1.519 (3)
N1—C1*A*	1.485 (3)	N3—C3*A*	1.474 (3)
C1*A*—C1*B*	1.529 (3)	C4—O4	1.224 (2)
C1*B*—O1*G*1	1.450 (2)	C4—N5	1.343 (2)
C1*B*—C1*G*2	1.517 (3)	C4—C4*A*	1.530 (3)
O1*G*1—C5	1.349 (2)	C4*A*—N4	1.452 (2)
C2—O2	1.240 (2)	C5—O5	1.195 (2)
C2—N3	1.329 (3)	C5—C5*A*	1.525 (3)
C2—C2*A*	1.532 (3)	N5—C5*A*	1.463 (2)
N2—C2*A*	1.460 (2)		
O1—C1—N2	125.0 (2)	C2—N3—C3*A*	126.6 (2)
O1—C1—C1*A*	120.5 (2)	N3—C3*A*—C3	110.9 (2)
N2—C1—C1*A*	114.3 (2)	O4—C4—N5	122.4 (2)
N1—C1*A*—C1	107.6 (2)	O4—C4—C4*A*	121.4 (2)
O2—C2—N3	120.8 (2)	N5—C4—C4*A*	116.2 (2)
O2—C2—C2*A*	119.4 (2)	N4—C4*A*—C4	110.6 (2)
N3—C2—C2*A*	119.8 (2)	C3—N4—C4*A*	126.8 (2)
C1—N2—C2*A*	121.8 (2)	O5—C5—O1*G*1	123.5 (2)
N2—C2*A*—C2	110.31 (15)	O5—C5—C5*A*	126.6 (2)
O3—C3—N4	119.5 (2)	O1*G*1—C5—C5*A*	109.8 (2)
O3—C3—C3*A*	119.5 (2)	C4—N5—C5*A*	118.2 (2)
N4—C3—C3*A*	120.9 (2)	N5—C5*A*—C5	111.4 (2)
C1—N2—C2*A*—C2	92.6 (2)	N3—C3*A*—C3—N4	138.4 (2)
C2—N3—C3*A*—C3	−77.1 (2)	N4—C4*A*—C4—N5	−165.4 (2)
C3—N4—C4*A*—C4	−112.2 (2)	C1*A*—C1—N2—C2*A*	162.0 (2)
C4—N5—C5*A*—C5	58.2 (2)	C2*A*—C2—N3—C3*A*	12.4 (3)
N1—C1*A*—C1—N2	162.5 (2)	C3*A*—C3—N4—C4*A*	−1.8 (3)
N2—C2*A*—C2—N3	−112.5 (2)	C4*A*—C4—N5—C5*A*	175.7 (2)

Table 3. *Hydrogen-bond geometry* (Å, °)

D	H	*A*	*D*—H	*D*—H···*A*
N1	H1*A*	O3^{i}	0.90 (2)	154 (2)
N1	H1*B*	O2*M*^{ii}	0.90 (2)	146 (2)
N1	H1*C*	Cl	0.90 (2)	159 (2)
N2	H2	Cl^{iii}	0.91 (3)	173 (2)
O2*M*	H2*M*	O1*S*	0.82 (1)	143 (5)
O2*M*′	H2*M*′	Cl^{iv}	0.84 (1)	169 (5)
O1*S*	H1*SA*	O2	0.88 (2)	170 (3)
O1*S*	H1*SB*	Cl^{iii}	0.88 (2)	164 (3)

Symmetry codes: (i) $1-x, y+\frac{1}{2}, \frac{3}{2}-z$; (ii) $x+1, y, z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (iv) $x-1, y, z$.

The peptide lactone (Fischer, 1982) was synthesized from the tetrapeptide H-D-Val-L-Pro-Sar-L-MeVal-OH (Brockmann & Lackner, 1968) and its condensation with (*Z*)-L-threonine followed by the cyclization of the (*Z*)-pentapeptide with acetyl chloride and imidazole. Hydrogenolytic deprotection of the (*Z*)-peptide lactone yielded the hydrochloride of the free cyclopeptide. Elemental analysis for $C_{23}H_{39}N_5O_6.HCl$: calculated C 53.32, H 7.78, Cl 6.84, N 13.53%; found C 53.33, H 7.76, Cl 6.75, N 13.46% (amorphous sample). Further details of the synthesis, NMR spectroscopic data and conformational properties in solution will be published elsewhere. Plate-shaped crystals were grown from diisopropylether/2-propanol/methanol at 277 K.

A single crystal was mounted on the tip of a glass fibre, coated with an inert oil and rapidly cooled to 153 K to prevent solvent loss. Data were collected with a learnt-profile method (Clegg, 1981). The structure was solved by direct methods using *SHELXS*90 (Sheldrick, 1990) and refined on F^2 by full-matrix least-squares techniques using *SHELXL*92 (Sheldrick, 1992). All non-H atoms were refined anisotropically. H atoms involved in bridging hydrogen bonds were refined freely with distance restraints for O—H and N—H bonds. The other H atoms were included at calculated positions and refined using a riding model.

The C3*G* atom of the proline was disordered. Two positions were refined with distance restraints for the 1—2 and 1—3 distances to occupancies of 0.65 and 0.35. The methanol molecule was found to be disordered. In the alternative location (45%), the positions of the C and the O atoms are approximately exchanged thus enabling a hydrogen bond from the O—H to the Cl. This part of the structure was refined with distance restraints for the C—O bond and rigid-bond restraints (Rollett, 1970; Hirshfeld, 1976; Trueblood & Dunitz, 1983), as well as similarity restraints for the anisotropic displacement parameters for neighbouring atoms.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*92 (Sheldrick, 1992).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71486 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1066]

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Structure of 2-(1-Acetoxy-2-fluoropropyl)-*N-tert*-butylbenzenesulfonamide

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Abstract

The structure of the title compound, $C_{15}H_{22}FNO_4S$ [2-(*N-tert*-butylsulfamoyl)-α-(1-fluoroethyl)benzyl acetate], has been determined from a single-crystal X-ray diffraction study. The torsion angles C(7)—O(1)—C(10)—O(2) [2.5 (3)°] and C(1)—S—N—H(N) [−62.6 (2)°], and an intramolecular hydrogen bond between the N atom and O(2) [2.979 (4) Å] stabilize the structure. The structure analysis confirms opposite configurations at C(7) and C(8). The absence of close contacts less than 3.269 (4) Å [C(11)···F] shows that the molecules are bound by van der Waals forces.

Comment

Sulfonamides have long been known in organic chemistry and have found extensive use in industrial and agricultural chemistry (March, 1985). Since the discovery (Levitt, 1977) of 2-substituted sulfonamide derivatives as highly active sulfonylurea herbicides having a low use rate, high degree of selectivity and excellent environmental safety, a number of sulfonamide compounds with 2-substituents have been widely investigated (Levitt, 1991). To date, the various known sulfonamide substituents are of relatively simple type and those with chiral centers have not been reported at all. In our research program, we have synthesized the title compound (I), which was an intermediate in the synthesis of a new herbicide (Kim, 1992), but faced some difficulties in clarifying the relative configuration of two chiral centers with