

80.18, H 5.99, N 6.45%; found: C 80.94, H 6.09, N 6.50%. Good single crystals of the latter, suitable for X-ray diffraction analysis, were obtained from slow evaporation of a solution of ethyl ether and *n*-pentane.

Crystal data

C₂₉H₂₆N₂O₂
M_r = 434.52
 Orthorhombic
*P*2₁2₁2₁
a = 8.205 (1) Å
b = 10.319 (1) Å
c = 27.168 (3) Å
V = 2300.2 (4) Å³
Z = 4
D_x = 1.255 Mg m⁻³
D_m not measured

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4334 measured reflections
 4038 independent reflections
 2882 reflections with
 $I > 2\sigma(I)$

Mo K α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 7.5$ – 12.5°
 $\mu = 0.079$ mm⁻¹
T = 293 (2) K
 Plate
 0.35 \times 0.20 \times 0.12 mm
 Colorless

*R*_{int} = 0.042
 $\theta_{\max} = 25^\circ$
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 32$
 2 standard reflections every 98 reflections
 intensity decay: <2%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.087$
 $S = 0.991$
 4038 reflections
 402 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.20P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.015$
 $\Delta\rho_{\max} = 0.11$ e Å⁻³
 $\Delta\rho_{\min} = -0.11$ e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = 1.6 (16)

Table 1. Selected torsion angles (°)

C14—C1—C2—N1	-71.5 (3)	C5—C7—C8—C9	-106.0 (3)
N1—C7—C8—C13	-41.4 (3)	C20—C1—C2—N1	163.7 (2)
C3—N1—C2—O1	166.7 (2)	C2—C1—C20—C21	-105.9 (3)
C3—N1—C2—C1	-16.5 (3)	C2—C1—C20—C29	75.6 (3)

The data set was collected with Mo K α radiation up to 50° in 2 θ . The structure was solved by direct methods and completed through successive cycles of ΔF synthesis, where all the H atoms in the structure were finally found. The resulting model was refined on *F*² using the whole data set, with anisotropic displacement factors for non-H atoms and an isotropic model for H atoms. The final ΔF synthesis proved remarkably featureless.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *MSCIAFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTLIPC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1223). Services for accessing these data are described at the back of the journal.

References

- Couderchet, M., Brozio, B. & Böger, P. (1986). *J. Pestic. Sci.* **11**, 611–617.
 Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Lotz, G. A., Palacios, S. M. & Rossi, R. A. (1994). *Tetrahedron Lett.* **35**, 7711–7714.
 Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Mulzer, J., Speck, T., Buschmann, J. & Luger, P. (1995). *Tetrahedron Lett.* **36**, 7643–7646.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Palacios, S. M., Vaccarini, C., Alonso, R. A. & Novo, R. (1995). *QSAR and Molecular Modeling: Concepts, Computational Tools and Biological Applications*, edited by F. Sanz, J. Giraldo & F. Manaut, pp. 180–183. Barcelona: Prous Science Publishers.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1994). *SHELXTLIPC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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2-(7-Ethylidene-6-methyl-1-oxa-4-thiaspiro-[4.5]dec-7-yl)ethanol

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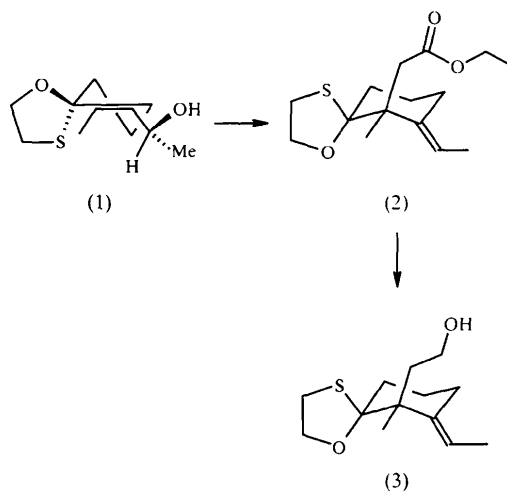
Abstract

The crystal of the title compound, C₁₃H₂₂O₂S, has two independent molecules in the asymmetric unit. The molecular dimensions are normal. Molecules are linked into chains along the *b* direction by O—H \cdots O hydrogen bonds, with O \cdots O distances of 2.655 (5) and 2.693 (5) Å.

Comment

In an investigation aimed at assessing the diastereoselectivity caused by an allylically positioned hemithioacetal in the orthoester Claisen rearrangement, we reacted al-

cohol (1) with triethylhemithioacetate. A single product, (2), was formed, which was reduced with lithium aluminium hydride to give a single alcohol, (3). The relative stereochemistry of (3) has been established by a single-crystal X-ray determination and is reported here; the structure of (1) was also established from an X-ray diffraction study of its carbinol epimer (Parvez *et al.*, 1997).



Since the starting material, (1), was a racemic mixture, the product of the rearrangement, (3), was also a mixture of two diastereomers. One of the two molecules in the asymmetric unit is shown in Fig. 1. The configurations at C3 and C4 in the molecule presented in Fig. 1 are *S* and *R*, respectively. Molecules with both *S,R* and *R,S* configurations are present in this centrosymmetric crystal; the *S,R* configuration was also chosen for the second molecule in the asymmetric unit. The molecular dimensions in both the molecules are within expected ranges, with similar corresponding

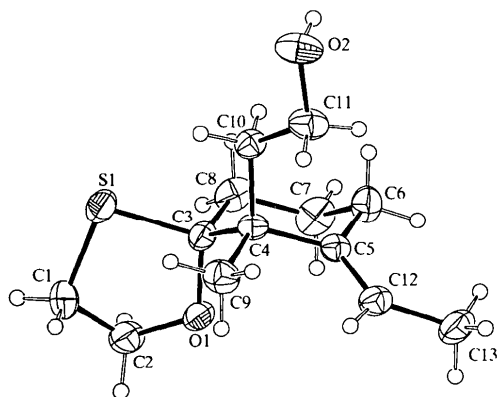


Fig. 1. ORTEP (Johnson, 1976) drawing of a molecule of (3) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms have been assigned an arbitrary radius.

bond distances and angles. In both molecules, S—C bond distances are inequivalent, with the distances of 1.800 (5) and 1.805 (5) Å being significantly shorter than the longer S—C distances of 1.861 (4) and 1.861 (5) Å. Similar inequivalent S—C bond distances have been reported in the crystal structures of cyclohexanespiro-2'-(1',3'-oxathiolan-5'-one 3'-oxide) (Frechina *et al.*, 1992), (+)-(3*S*,4*R*)-6-phenyl-1-oxa-4-thiaspiro[4.5]decan-8-one (Sonoda *et al.*, 1992) and two derivatives of an oxathia-spiro-decene (Parvez *et al.*, 1997).

The five-membered heterocyclic rings in the two molecules adopt C2- and C15-envelope conformations, with atoms C2 and C15 displaced by 0.569 (8) and 0.568 (8) Å, respectively, out of the planes of the remaining atoms of their respective rings. The C3—C8 and C16—C21 six-membered rings are in classical chair conformations.

There are short intermolecular hydrogen bonds involving hydroxy groups of adjacent molecules, with O···O separations of 2.693 (5) and 2.655 (5) Å, linking the molecules along the *b* axis; details are given in Table 2.

Experimental

The alcohol (1) was reacted with triethylhemithioacetate in boiling toluene until it had completely disappeared (6–7 h), to yield a single product, (2), which was reduced with lithium aluminium hydride in Et₂O in an ice bath to give a single alcohol, (3). Crystals of (3) (m.p. 379 K) suitable for X-ray crystallographic study were grown by slow evaporation from a mixture of CCl₄ and petroleum ether (b.p. 333–353 K) at room temperature.

Crystal data

C₁₃H₂₂O₂S
M_r = 242.37
 Monoclinic
*P*2₁/*c*
a = 12.435 (3) Å
b = 7.517 (3) Å
c = 28.790 (4) Å
 β = 93.344 (17)°
V = 2686.5 (13) Å³
Z = 8
D_x = 1.198 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 9.0–15.0°
 μ = 0.226 mm⁻¹
T = 293 (1) K
 Prism
 0.50 × 0.29 × 0.21 mm
 Colourless

Data collection

Rigaku AFC-6*S* diffractometer
 ω -2 θ scans
 Absorption correction:
 ψ scans (North *et al.*, 1968)
 T_{\min} = 0.977, T_{\max} = 1.000
 6475 measured reflections
 6199 independent reflections

2072 reflections with
 $I > 2\sigma(I)$
 R_{int} = 0.058
 θ_{max} = 27.6°
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 9$
 $l = -37 \rightarrow 37$
 3 standard reflections
 every 200 reflections
 intensity decay: 0.17%

RefinementRefinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.056$$

$$wR(F^2) = 0.187$$

$$S = 1.033$$

6199 reflections

296 parameters

H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.026P)^2$$

$$+ 5.43P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.01$$

$$\Delta\rho_{\max} = 0.263 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.292 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

S1—C1	1.805 (5)	S2—C14	1.800 (5)
S1—C3	1.861 (5)	S2—C16	1.861 (4)
O1—C2	1.423 (5)	O3—C15	1.420 (5)
O1—C3	1.426 (5)	O3—C16	1.437 (5)
O2—C11	1.421 (5)	O4—C24	1.425 (5)
C1—S1—C3	92.4 (2)	C14—S2—C16	92.0 (2)
C2—O1—C3	111.7 (4)	C15—O3—C16	111.6 (3)
C2—C1—S1	103.6 (4)	C15—C14—S2	104.1 (4)
O1—C3—S1	105.9 (3)	O3—C16—S2	105.9 (3)
C8—C3—S1	108.4 (3)	C21—C16—S2	108.7 (3)
C4—C3—S1	112.6 (3)	C17—C16—S2	113.2 (3)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2...O4 ⁱ	0.82	1.89	2.693 (5)	166.4
O4—H4...O2 ⁱⁱ	0.82	1.85	2.655 (5)	166.9

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

The space group $P2_1/c$ was determined uniquely from the systematic absences. The H atoms were located from a difference map and were allowed to ride at geometrically idealized positions, with C—H and O—H distances of 0.95 and 0.82 \AA , respectively.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL97*.

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References

- Fan, H.-F. (1991). *SAPI91. Structure Analysis Program with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Frechina, J. V., Sanz, V., Cervilla, A., Ramirez, J. A., Ghilardi, C. A. & Orlandini, A. (1992). *Acta Cryst.* **C48**, 1523–1525.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1994). *TEXSAN Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Parvez, M., Jeyaraj, D. A. & Yadav, V. K. (1997). *Acta Cryst.* **C53**, 1961–1963.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sonoda, S., Houchigai, H., Asaoka, M. & Takei, H. (1992). *Tetrahedron Lett.* **33**, 3145–3146.

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Methyl *N*-(*tert*-Butoxycarbonyl)glycyl-L-valyl-L-tryptophanate

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Abstract

The title compound, $C_{24}H_{34}N_4O_6$, is an end-protected tripeptide and the peptide backbone adopts an extended conformation. The peptide units are *trans* and show significant deviations from planarity. The crystal packing enables neighbouring molecules to interact through an antiparallel β -sheet arrangement. An intramolecular hydrogen bond occurs between the peptide backbone carbonyl group and the N atom in the tryptophan side chain. An interesting feature of the packing is that the tryptophan side chain straddles both hydrophobic and hydrophilic environments.

Comment

The observed bond geometry of the title tripeptide, (I), agrees with expectations. All the peptide units are *trans* and show significant deviations from planarity. The conformation of the butoxycarbonyl (BOC) group, characterized by the torsion angles θ_0 (C1—O1—C0'—N1) and ω_0 (O1—C0'—N1—CA) is *trans-trans* (Benedetti *et al.*, 1980). The peptide chain backbone torsion angles are $\varphi_1 = 108.8(5)$, $\psi_1 = 167.8(4)$, $\omega_1 = 173.5(4)$, $\varphi_2 = -106.4(5)$, $\psi_2 = 115.3(4)$, $\omega_2 = -169.6(4)$, $\varphi_3 = -100.0(5)$, $\psi_3 = -29.6(6)$ and $\omega_3 = -176.0(5)^\circ$, and represent an extended