

Fig. 1. ORTEP (Johnson, 1976) drawing of (4*S*,5*S*,7*S*,8*S*)-11-hydroxy-1(10-guaien-8-yl) (1*S*)-1-phenylethylcarbamate. The thermal ellipsoids for non-H atoms are drawn at 50% probability level.

N(20'). Final atomic coordinates and isotropic or equivalent isotropic displacement parameters of non-H atoms are listed in Table 1.* Bond distances

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53861 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1991). C47, 1561–1563

Structure of a Model for Aspirochlorine (Antibiotic A30641)

BY KEVIN A. ANDERSEN AND OREN P. ANDERSON*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

(Received 17 April 1990; accepted 2 January 1991)

Abstract. (1) $C_{20}H_{18}N_2O_5S_2$, $M_r = 430.48$, monoclinic, $P2_1/c$, $a = 9.934$ (3), $b = 18.730$ (5), $c = 10.563$ (2) Å, $\beta = 96.23$ (2)°, $V = 1954$ (1) Å³, $Z = 4$, $D_x = 1.46$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 3.0$ cm⁻¹, $F(000) = 896$, $T = 112$ K, $R = 0.046$ ($wR = 0.041$) for 2813 unique, observed reflections. The

and angles are given in Table 2. A perspective drawing of one of the molecules is shown in Fig. 1 giving the atomic numbering scheme.

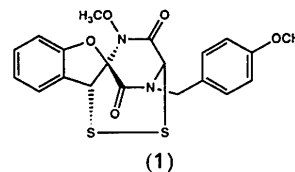
Related literature. In a chemotaxonomic study of the genus *Thapsia* the distribution of sesquiterpenes and sesquiterpene lactones was investigated (Smitt, 1991). Within the species *Thapsia villosa* var. minor morphological as well as phytochemical differences were revealed. The occurrence of three new compounds, which are monoesters of a sesquiterpene diol with a guaian skeleton, in only some specimens is of chemotaxonomic value (Lemmich, Smitt, Jensen & Christensen, 1991). The structure of the three compounds was elucidated by spectroscopic methods, but it was not possible to establish the relative configuration at all the chiral centres in the sesquiterpene moiety from the NMR spectroscopic data.

The authors wish to thank Mr Fleming Hansen and Dr Birthe Jensen for technical assistance in the experimental crystallographic work.

References

- ALLINGER, N. L. & SPRAGUE, P. W. (1972). *J. Am. Chem. Soc.* **94**, 5734–5747.
 Cambridge Structural Database (1989). Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.
 Enraf-Nonius (1981). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 JOHNSON, C. K. (1976). ORTEP. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 LEMMICH, E., SMITT, U. W., JENSEN, J. S. & CHRISTENSEN, S. B. (1991). In preparation.
 SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 SMITT, U. W. (1991). To be published.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

compound is a model for aspirochlorine (antibiotic A30641).



(1)

* To whom correspondence should be addressed.

Table 1. Atomic coordinates and isotropic thermal parameters (Å²) for (1), with e.s.d.'s in parentheses

	U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.			U_{iso}
	x	y	z	
S(1)	0.6609 (1)	1.0121 (1)	0.6434 (1)	0.025 (1)
S(2)	0.7641 (1)	0.9897 (1)	0.4896 (1)	0.025 (1)
O(1)	0.7055 (2)	0.8399 (1)	0.8494 (2)	0.020 (1)
O(2)	0.7561 (2)	0.7602 (1)	0.6473 (2)	0.024 (1)
O(3)	0.8703 (2)	0.9494 (1)	0.9059 (1)	0.024 (1)
O(4)	1.0203 (2)	0.9998 (1)	0.7246 (2)	0.028 (1)
O(5)	1.4728 (2)	0.8124 (1)	0.4589 (2)	0.027 (1)
N(1)	0.8682 (2)	0.9178 (1)	0.7854 (2)	0.019 (1)
N(2)	0.8569 (2)	0.8535 (1)	0.5560 (2)	0.018 (1)
C(1)	0.6175 (3)	0.9223 (1)	0.6878 (2)	0.019 (1)
C(2)	0.5339 (3)	0.9216 (1)	0.7978 (2)	0.019 (1)
C(3)	0.4175 (3)	0.9582 (1)	0.8192 (2)	0.026 (1)
C(4)	0.3590 (3)	0.9439 (2)	0.9303 (2)	0.031 (1)
C(5)	0.4169 (3)	0.8936 (1)	1.0163 (3)	0.031 (1)
C(6)	0.5344 (3)	0.8567 (1)	0.9961 (2)	0.025 (1)
C(7)	0.5897 (3)	0.8727 (1)	0.8856 (2)	0.019 (1)
C(8)	0.7447 (3)	0.8769 (1)	0.7424 (2)	0.017 (1)
C(9)	0.9542 (3)	0.9076 (2)	0.9981 (2)	0.036 (1)
C(10)	0.9363 (3)	0.9535 (1)	0.6993 (2)	0.020 (1)
C(11)	0.8959 (3)	0.9287 (1)	0.5640 (2)	0.020 (1)
C(12)	0.7862 (3)	0.8227 (1)	0.6441 (2)	0.019 (1)
C(13)	0.9002 (3)	0.8125 (1)	0.4497 (2)	0.021 (1)
C(14)	1.0531 (3)	0.8108 (1)	0.4517 (2)	0.019 (1)
C(15)	1.1108 (3)	0.8130 (1)	0.3384 (2)	0.023 (1)
C(16)	1.2507 (3)	0.8122 (1)	0.3361 (2)	0.022 (1)
C(17)	1.3335 (3)	0.8107 (1)	0.4490 (2)	0.021 (1)
C(18)	1.2781 (3)	0.8093 (1)	0.5642 (2)	0.024 (1)
C(19)	1.1388 (3)	0.8086 (1)	0.5642 (2)	0.024 (1)
C(20)	1.5336 (3)	0.8123 (2)	0.3423 (3)	0.032 (1)

Table 2. Bond lengths (Å) and bond angles for (1), with e.s.d.'s in parentheses

S(1)—S(2)	2.056 (1)	S(1)—C(1)	1.812 (2)
S(2)—C(11)	1.848 (2)	O(1)—C(7)	1.393 (3)
O(1)—C(8)	1.416 (3)	O(2)—C(12)	1.210 (3)
O(3)—N(1)	1.402 (2)	O(3)—C(9)	1.442 (3)
O(4)—C(10)	1.213 (3)	O(5)—C(17)	1.377 (3)
O(5)—C(20)	1.430 (3)	N(1)—C(8)	1.475 (3)
N(1)—C(10)	1.366 (3)	N(2)—C(11)	1.461 (3)
N(2)—C(12)	1.354 (3)	N(2)—C(13)	1.463 (3)
C(1)—C(2)	1.500 (4)	C(1)—C(8)	1.578 (3)
C(2)—C(3)	1.384 (4)	C(2)—C(7)	1.377 (3)
C(3)—C(4)	1.391 (4)	C(4)—C(5)	1.388 (4)
C(5)—C(6)	1.393 (4)	C(6)—C(7)	1.375 (4)
C(8)—C(12)	1.540 (3)	C(10)—C(11)	1.516 (3)
C(13)—C(14)	1.517 (4)	C(14)—C(15)	1.383 (4)
C(14)—C(19)	1.386 (3)	C(15)—C(16)	1.393 (4)
C(16)—C(17)	1.373 (3)	C(17)—C(19)	1.390 (4)
C(18)—C(19)	1.384 (4)		
S(2)—S(1)—C(1)	99.7 (1)	S(1)—S(2)—C(11)	100.4 (1)
C(7)—O(1)—C(8)	108.1 (2)	N(1)—O(3)—C(9)	109.6 (2)
C(17)—O(5)—C(20)	116.7 (2)	O(3)—N(1)—C(8)	115.4 (2)
O(3)—N(1)—C(10)	115.9 (2)	C(8)—N(1)—C(10)	120.3 (2)
C(11)—N(2)—C(12)	121.6 (2)	C(11)—N(2)—C(13)	116.9 (2)
C(12)—N(2)—C(13)	121.4 (2)	S(1)—C(1)—C(2)	112.1 (2)
S(1)—C(1)—C(8)	113.0 (2)	C(2)—C(1)—C(8)	101.6 (2)
C(1)—C(2)—C(3)	131.7 (2)	C(1)—C(2)—C(7)	108.1 (2)
C(3)—C(2)—C(7)	120.2 (2)	C(2)—C(3)—C(4)	118.3 (2)
C(3)—C(4)—C(5)	120.1 (3)	C(4)—C(5)—C(6)	122.0 (3)
C(5)—C(6)—C(7)	116.2 (2)	O(1)—C(7)—C(2)	113.1 (2)
O(1)—C(7)—C(6)	123.7 (2)	C(2)—C(7)—C(6)	123.1 (2)
O(1)—C(8)—N(1)	107.4 (2)	O(1)—C(8)—C(1)	106.0 (2)
N(1)—C(8)—C(1)	116.1 (2)	O(1)—C(8)—C(12)	109.4 (2)
N(1)—C(8)—C(12)	105.9 (2)	C(1)—C(8)—C(12)	111.8 (2)
O(4)—C(10)—N(1)	125.7 (2)	O(4)—C(10)—C(11)	122.2 (2)
N(1)—C(10)—C(11)	112.2 (2)	S(2)—C(11)—N(2)	113.6 (2)
S(2)—C(11)—C(10)	108.3 (2)	N(2)—C(11)—C(10)	113.1 (2)
O(2)—C(12)—N(2)	125.4 (2)	O(2)—C(12)—C(8)	122.2 (2)
N(2)—C(12)—C(8)	112.3 (2)	N(2)—C(13)—C(14)	112.2 (2)
C(13)—C(14)—C(15)	119.7 (2)	C(13)—C(14)—C(19)	122.3 (2)
C(15)—C(14)—C(19)	118.0 (2)	C(14)—C(15)—C(16)	121.5 (2)
C(15)—C(16)—C(17)	119.4 (2)	O(5)—C(17)—C(16)	124.6 (2)
O(5)—C(17)—C(18)	115.1 (2)	C(16)—C(17)—C(18)	120.2 (2)
C(17)—C(18)—C(19)	119.5 (2)	C(14)—C(19)—C(18)	121.4 (2)

Experimental. Crystals (colorless prisms) of (1) obtained from an ethyl acetate/hexane solution by Greg Miknis and Professor R. Williams (Colorado State University). Crystal size 0.18 × 0.26 × 0.14 mm. Nicolet R3m diffractometer, unit-cell constants from least-squares fit of setting angles for 25 reflections ($2\theta_{av} = 18.30^\circ$). Data collected ($\theta/2\theta$ scans) to $(\sin\theta)/\lambda = 0.5947 \text{ \AA}^{-1}$, $0 \leq h \leq 13$, $0 \leq k \leq 23$, $-13 \leq l \leq 13$. Three standard reflections (500, 060, 002) every 97, no change in intensity; Lorentz and polarization corrections, no absorption correction applied due to low absorption coefficient; 3440 unique reflections, $R_{int} = 0.014$, 2813 reflections with $F_o > 2.5\sigma(F_o)$ observed.

Structure solved by direct methods (SOLV; Sheldrick, 1985); block diagonal (max. 103 parameters/block, 268 parameters total, data/parameters = 10.50) weighted $\{w = [\sigma^2(F) + gF^2]^{-1}$, $g = 1.70 \times 10^{-4}\}$ least-squares refinement on F . H atoms in idealized positions [C—H = 0.96 Å, $U(H) = 1.2 \times U_{iso}(C)$]; non-H atoms refined with anisotropic thermal parameters; methyl groups treated as idealized rigid rotors. At convergence $[(\Delta/\sigma)_{max} = 0.055$, $(\Delta/\sigma)_{mean} = 0.015$ for last 3 cycles] $R = 0.046$, $wR = 0.041$, $S = 1.38$, slope of normal probability plot = 1.22, $(\Delta\rho)_{max} = 0.35$, $(\Delta\rho)_{min} = -0.27 \text{ e \AA}^{-3}$. Neutral-atom scattering factors and anomalous-dispersion corrections used (International Tables for

X-ray Crystallography, 1974, Vol. IV); all calculations performed using SHELXTL program library (Sheldrick, 1985). Table 1 lists the atomic coordinates and Table 2 gives bond lengths and angles.* Fig. 1 shows the structure of (1), as well as the numbering scheme used.

Related literature. The structure of *O,O*-dimethyl-*aspirochlorine* (2) has been previously studied (Sakata, Maruyama, Uzawa, Sakurai, Lu & Clardy, 1987). The structures of (1) and (2) are similar, except that an amide linkage occurs within the ring system of (1) [C(12)—N(2)] in place of the methoxy-substituted imine linkage in (2). Peripheral substituents on the main three-ring system also differ. In

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53882 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

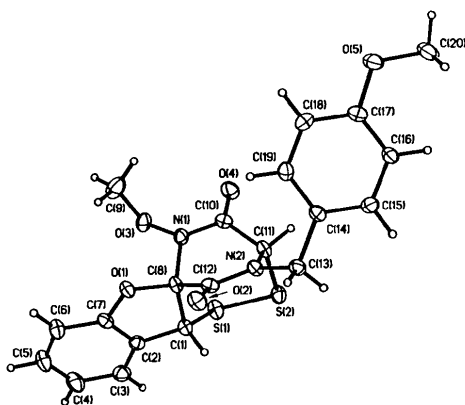


Fig. 1. The structure of (1) with atomic labeling scheme. 50% probability thermal ellipsoids.

Acta Cryst. (1991). **C47**, 1563–1566

Structure of 18'-Epivinblastine

BY VINCENT M. LYNCH, ANDREW STAMFORD, PHILIP MAGNUS AND BRIAN E. DAVIS

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA

(Received 1 October 1990; accepted 2 January 1991)

Abstract. Methyl {3a*R*-[3a α ,4 β ,5 β ,5a β ,9(3*R**,-5*S**,7*R**,9*R**),10*bR*,13a α]}-4-(acetyloxy)-3a-ethyl-9-[5-ethyl-1,4,5,6,7,8,9,10-octahydro-5-hydroxy-9-(methoxycarbonyl)-2*H*-3,7-methanoazacycloundecino[5,4-*b*]indol-9-yl]-3a,4,5,5a,6,11,12,13a-octahydro-5-hydroxy-8-methoxy-6-methyl-1*H*-indolizino[8,1-*c,d*]carbazole-5-carboxylate methanol solvate, C₄₆H₅₈N₄O₉ · 2CH₃OH (1), *M_r* = 875.07, monoclinic, *P*2₁, *a* = 10.2759 (12), *b* = 22.353 (3), *c* = 10.4051 (12) Å, β = 106.502 (9)°, *V* = 2291.6 (5) Å³, *Z* = 2, *D_x* = 1.27 g cm⁻³, Mo *K* α radiation, λ = 0.7107 Å, μ = 0.8397 cm⁻¹, *F*(000) = 940, *T* = 198 K, *R* = 0.0470 for 2751 reflections, *F_o* \geq 4 σ (*F_o*). The *C* ring of the vindoline moiety is in the boat conformation with the hydroxy group and the tertiary N in the bowsprit positions resulting in a fairly short intramolecular hydrogen-bonding interaction. The relevant parameters for O3—H3···N9 are O···N 2.651 (6), H···N 1.94 (5) Å and O—H···N 147 (5)°. The *D* and *E* rings are in the sofa and envelope conformations, respectively. The piperidine ring of the catharanthine portion of the molecule assumes the chair conformation while the conformation of the azacyclononene ring is a boat-chair. An intramolecular hydrogen bond between the indolino NH of the catharanthine moiety and methoxy O (O25) of the vindoline moiety is also observed. The relevant parameters for N16'—H16'···O25 are N···O 2.827 (6), H···N2.14 (6) Å and O—H···N 136 (5)°.

0108-2701/91/071563-04\$03.00

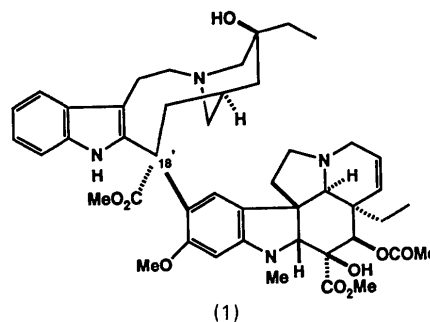
(1), the angles about each S atom are significantly smaller than in (2) [99.7 (1) at S(1), 100.4 (1)° at S(2), 100.5 and 101.7° at analogous atoms in (2)], and the disulfide bond is significantly longer in (1) [2.056 (1) Å] than in (2) (2.025 Å).

We acknowledge the support of the US National Science Foundation for the purchase of the Nicolet R3m diffractometer and computing system.

References

- SAKATA, K., MARUYAMA, M., UZAWA, J., SAKURAI, A., LU, H. S. M. & CLARDY, J. (1987). *Tetrahedron Lett.* **28**, 5607–5610.
SHELDRIK, G. M. (1985). *SHELXTL Users Manual*. Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Experimental. (1) was prepared during the course of a synthesis of the clinically important antitumor alkaloid vinblastine (Moncrief & Lipscomb, 1965; Magnus, Stamford & Ladlow, 1991). The absolute



configuration of (1) was assigned on the basis of internal comparison to the vindoline moiety (Moncrief & Lipscomb, 1966). Colorless crystals were obtained by slow evaporation of a methanol-water solution. The data crystal was separated from a cluster of smaller crystals and had approximate dimensions 0.17 × 0.34 × 0.43 mm. The data were collected on a Nicolet P3 diffractometer using a graphite monochromator and equipped with a Nicolet LT-2 low-temperature device. The lattice parameters were obtained by the least-squares refinement of 40 reflections with 18.2 < 2 θ < 21.2°.

© 1991 International Union of Crystallography