References

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Csöregh, I., Czugler, M., Törnroos, K. W., Weber, E. & Ahrendt, J. (1989). *J. Chem. Soc. Perkin Trans.* 2, pp. 1491–1497.

Gdaniec, M., Gilski, M. & Denisov, G. S. (1994). *Acta Cryst.* **C50**, 1622–1626.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Gupta, M. P. & Mahata, A. P. (1975). *Cryst. Struct. Commun.* **4**, 37–40.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1996). C**52**, 1272–1274

A Pyrazoline Derivative of Eunicin Acetate

Safia Khalil,[a] M. Bilayet Hossain,[a] Dick van der Helm,[a]* Maktoob Alam[b] and Radhika Sanduja[b]

[a]*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, USA, and* [b]*College of Pharmacy, University of Houston, Houston, Texas 77204, USA*

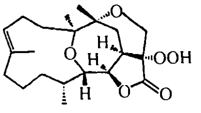
(*Received 17 July 1995; accepted 27 November 1995*)

Abstract

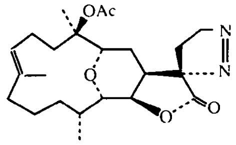
The present crystal structure determination established spiro[{3a,4,5,6,7,8,11,12,13,14,15,15a-dodecahydro-6,10,14-trimethyl-2-oxo-5,15-epoxy-3*H*-cyclotetradeca[*b*]furan}-3,3′-1′-pyrazoline]-6-yl acetate, $C_{23}H_{34}N_2O_5$, as a pyrazoline derivative of eunicin acetate. The spiro substitution of the pyrazoline ring causes elongation of the bonds within the lactone ring and also shortening of the carbonyl bond. The cembranolide skeleton is slightly more bent than that observed in the parent eunicin molecule.

Comment

During the extraction, isolation and structure determination of a novel cembranoid planaxool, (I), obtained from the mollusk *Planaxis sulcatus* (Alam *et al.*, 1993), one of the samples derived from an extract that had been stored in a polypropylene-lined drum was found to contain an additional chromatographic peak. Isolation of the compound responsible for this peak, using high-performance liquid chromatography (HPLC), gave a colorless compound, (II). The crystal structure was determined in order to properly identify the compound.



(I)



(II)

A perspective *ORTEP*II plot (Johnson, 1976) of the title molecule is shown in Fig. 1, which also shows the atom-numbering scheme. The X-ray structure established the compound as a pyrazoline derivative of eunicin acetate. The absolute configuration of the molecule was not determined but assigned according to that of eunicin (Hossain, Nicholas & van der Helm, 1968) and other cembranolides, the absolute configurations of which were determined by X-ray diffraction (van der Helm, Enwall, Weinheimer, Karns & Ciereszko, 1976; Ealick, van der Helm & Weinheimer, 1975; Chang, Ciereszko, Hossain & van der Helm, 1980). The bond distances and angles are in general agreement with those observed in eunicin iodoacetate (Weinheimer, Middlebrook, Bledsoe, Marsico & Karns, 1968; Hossain, Nicholas & van der Helm, 1968) and other cembranolides (van der Helm, Enwall, Weinheimer, Karns & Ciereszko, 1976; Ealick, van der Helm & Weinheimer, 1975; Chang, Ciereszko, Hossain & van der Helm,

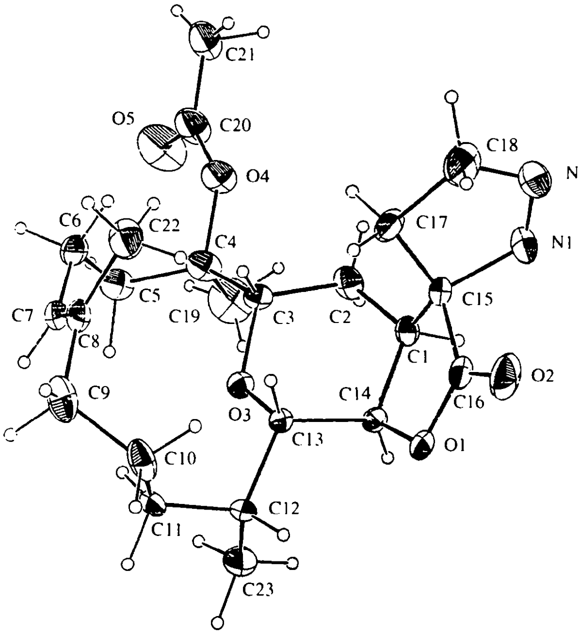


Fig. 1. The molecular structure of compound (II) showing 50% probability displacement ellipsoids.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

1980; Sen Gupta, Hossain & van der Helm, 1986). The effect of pyrazoline substitution is evident in the bond-length elongation in the lactone ring. The carbonyl bond (C16═O2) is shortened significantly [1.188 (6) Å in (II) compared with 1.26 (1) Å in eunicin iodoacetate]. The r.m.s. difference of the endocyclic torsion angles of eunicin and (II) is less than 4° (Table 2). The cembranolide skeleton is more folded in the present compound than in eunicin, the dihedral angle between the cembrane ring and the lactone ring being 78 (1)° compared with 84 (2)° in eunicin acetate. The pyrazoline ring is planar and its plane is nearly perpendicular to the plane of the lactone ring [dihedral angle 86 (1)°]. The C—H distances range between 0.76 (9) and 1.11 (6) Å.

The mollusk *Planaxis sulcatus* was found to contain a small amount of eunicin. It is possible that compound (II) is an artifact derived from eunicin by the action of stabilizers used in the preparation of polypropylene. Compound (II) could also be synthesized by treating eunicin with diazomethane. Preparation of an analogous pyrazoline derivative of cueunicin acetate, obtained by treating cueunicin with diazomethane, has been reported (Weinheimer, Chang & Matson, 1979).

Experimental

The title compound was crystallized from $CHCl_3$/methanol solution.

Crystal data

$C_{23}H_{34}N_2O_5$
$M_r = 418.6$
Orthorhombic
$P2_12_12_1$
$a = 9.045\ (1)$ Å
$b = 29.148\ (3)$ Å
$c = 8.6766\ (3)$ Å
$V = 2287.5\ (2)$ Å^3
$Z = 4$
$D_x = 1.215$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 48 reflections
$\theta = 20$–$38°$
$\mu = 0.59$ mm^{-1}
$T = 163$ K
Plate
0.30 × 0.13 × 0.03 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2450 measured reflections
2232 independent reflections
1768 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 75°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 36$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: 2.3%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.048$
$S = 1.5$
1768 reflections
407 parameters
H atoms located from a difference Fourier map and refined isotropically

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: none
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)*

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

	x	y	z	$U_{\rm eq}$
O1	0.3530 (3)	0.79429 (8)	0.5134 (4)	0.042 (1)
O2	0.1975 (3)	0.7668 (1)	0.6894 (5)	0.064 (1)
O3	0.6696 (2)	0.87249 (8)	0.5216 (5)	0.0315 (9)
O4	0.9056 (3)	0.8753 (1)	0.8504 (4)	0.055 (1)
O5	1.1475 (4)	0.8942 (2)	0.8439 (6)	0.107 (2)
N1	0.4604 (5)	0.7349 (1)	0.8396 (6)	0.056 (2)
N2	0.4138 (6)	0.7371 (1)	0.9731 (7)	0.077 (2)
C1	0.5812 (4)	0.7860 (1)	0.6457 (5)	0.034 (1)
C2	0.7231 (5)	0.8096 (1)	0.6943 (7)	0.043 (2)
C3	0.7239 (4)	0.8613 (1)	0.6713 (5)	0.031 (1)
C4	0.8807 (4)	0.8829 (2)	0.6841 (6)	0.048 (2)
C5	0.8843 (5)	0.9336 (2)	0.6514 (7)	0.052 (2)
C6	0.7874 (5)	0.9649 (2)	0.7501 (7)	0.052 (2)
C7	0.6496 (5)	0.9807 (1)	0.6721 (6)	0.043 (2)
C8	0.5096 (5)	0.9765 (1)	0.7156 (6)	0.043 (2)
C9	0.3840 (6)	0.9901 (2)	0.6100 (8)	0.061 (2)
C10	0.3272 (5)	0.9495 (1)	0.5155 (7)	0.050 (2)
C11	0.4355 (5)	0.9353 (1)	0.3914 (6)	0.041 (2)
C12	0.4544 (5)	0.8831 (1)	0.3632 (5)	0.038 (2)
C13	0.5178 (4)	0.8601 (1)	0.5066 (5)	0.027 (1)
C14	0.5077 (4)	0.8077 (1)	0.5052 (6)	0.033 (1)
C15	0.4538 (4)	0.7812 (1)	0.7608 (5)	0.035 (1)
C16	0.3183 (5)	0.7793 (1)	0.6560 (6)	0.040 (2)
C17	0.4329 (6)	0.8150 (2)	0.8905 (6)	0.049 (2)
C18	0.3680 (9)	0.7835 (2)	1.0151 (9)	0.081 (3)
C19	0.9905 (6)	0.8574 (3)	0.579 (1)	0.079 (3)
C20	1.0386 (6)	0.8833 (2)	0.9146 (8)	0.073 (3)
C21	1.028 (1)	0.8797 (3)	1.084 (1)	0.088 (3)
C22	0.4637 (7)	0.9556 (2)	0.8673 (7)	0.056 (2)
C23	0.5508 (8)	0.8756 (2)	0.2237 (7)	0.065 (2)

Table 2. *Selected geometric parameters (Å, °) and comparison of torsion angles (°) with those of eunicin*

O1—C14	1.455 (5)	C4—C5	1.506 (7)
O1—C16	1.349 (6)	C4—C19	1.542 (9)
O2—C16	1.188 (6)	C5—C6	1.528 (7)
O3—C3	1.426 (5)	C6—C7	1.491 (7)
O3—C13	1.425 (4)	C7—C8	1.327 (7)
O4—C4	1.477 (6)	C8—C9	1.513 (8)
O4—C20	1.347 (7)	C8—C22	1.509 (8)
O5—C20	1.203 (8)	C9—C10	1.530 (7)
N1—N2	1.234 (8)	C10—C11	1.514 (7)
N1—C15	1.516 (5)	C11—C12	1.549 (5)
N2—C18	1.461 (8)	C12—C13	1.526 (6)
C1—C2	1.516 (6)	C12—C23	1.508 (8)
C1—C14	1.526 (6)	C13—C14	1.530 (5)
C1—C15	1.531 (6)	C15—C16	1.527 (6)
C2—C3	1.523 (3)	C15—C17	1.507 (7)
C3—C4	1.555 (5)	C17—C18	1.535 (9)
C20—C21	1.475 (12)		
C2—C1—C14	113.7 (3)	C13—C14—O1	109.0 (3)
C2—C1—C15	119.9 (4)	C1—C14—O1	105.6 (3)
C14—C1—C15	103.4 (3)	C14—O1—C16	110.8 (3)
C1—C2—C3	114.6 (3)	C1—C15—C16	102.6 (4)
C2—C3—C4	113.3 (3)	C1—C15—C17	121.5 (3)
C2—C3—O3	110.1 (4)	C1—C15—N1	110.2 (3)
C4—C3—O3	106.7 (3)	C16—C15—C17	111.6 (4)
C3—C4—C5	113.8 (3)	C16—C15—N1	105.5 (3)
C3—C4—O4	98.5 (3)	N1—C15—C17	104.5 (4)
C5—C4—O4	109.2 (4)	C15—C16—O1	110.4 (3)
C3—C4—C19	110.5 (4)	C15—C16—O2	127.1 (5)
C5—C4—C19	110.5 (4)	O1—C16—O2	122.5 (5)
O4—C4—C19	114.2 (4)	C15—C17—C18	100.5 (4)

C4—C5—C6	117.9 (4)	C17—C18—N2	105.7 (6)
C5—C6—C7	114.2 (5)	C15—N1—N2	111.3 (4)
C6—C7—C8	129.8 (5)	C9—C10—C11	112.0 (4)
C7—C8—C9	121.4 (5)	C10—C11—C12	116.9 (4)
C7—C8—C22	123.2 (3)	O4—C20—C21	110.0 (6)
C9—C8—C22	115.3 (3)	C11—C12—C13	110.1 (4)
C8—C9—C10	111.9 (4)	O4—C20—O5	124.5 (6)
C12—C13—C14	114.2 (4)	C11—C12—C23	109.5 (4)
C12—C13—O3	109.0 (3)	O5—C20—C21	125.5 (6)
C14—C13—O3	108.1 (3)	C13—C12—C23	111.9 (4)
C3—O3—C13	110.9 (3)	C4—O4—C20	121.0 (4)
C13—C14—C1	112.5 (4)	N1—N2—C18	112.3 (5)

	(II)	Eunicin†
C1—C2—C3—C4	−166.1 (4)	−168
C2—C3—C4—C5	176.3 (5)	179
C3—C4—C5—C6	57.8 (6)	57
C4—C5—C6—C7	−102.8 (5)	−107
C5—C6—C7—C8	123.8 (5)	128
C6—C7—C8—C9	−172.7 (4)	−173
C7—C8—C9—C10	93.3 (5)	99
C8—C9—C10—C11	−71.9 (6)	−77
C9—C10—C11—C12	140.5 (4)	141
C10—C11—C12—C13	−63.6 (5)	−68
C11—C12—C13—C14	166.6 (4)	170
C12—C13—C14—C1	176.3 (3)	172
C13—C14—C1—C2	−38.8 (5)	−37
C14—C1—C2—C3	34.9 (6)	37
C1—C14—O1—C16	17.0 (4)	22
C14—O1—C16—C15	−0.4 (6)	−3
O1—C16—C15—C1	−16.2 (4)	−18
C16—C15—C1—C14	25.0 (3)	27
C15—C1—C14—O1	−26.1 (4)	−30

† E.s.d.'s for the torsion angles of eunicin are in the range 1–2°.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: local least-squares cell program. Data reduction: local data reduction program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1984). Molecular graphics: *ORTEP*II (Johnson, 1976).

This work was partially supported by NIH grant 17562 (DvdH).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1181). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alam, M., Martin, G. E., Zektzer, A. S., Weinheimer, A. J., Sanduja, R. & Ghuman, M. A. (1993). *J. Nat. Prod.* **56**, 774–779.

Chang, C. Y., Ciereszko, L. S., Hossain, M. B. & van der Helm, D. (1980). *Acta Cryst.* B**36**, 731–733.

Ealick, S. E., van der Helm, D. & Weinheimer, A. J. (1975). *Acta Cryst.* B**31**, 1618–1626.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Hossain, M. B., Nicholas, A. F. & van der Helm, D. (1968). *Chem. Commun.* pp. 385–386.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sen Gupta, P. K., Hossain, M. B. & van der Helm, D. (1986). *Acta Cryst.* C**42**, 434–436.

Sheldrick, G. M. (1984). *SHELX*76. *Program for Crystal Structure Determination*. University of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

van der Helm, D., Enwall, E. L., Weinheimer, A. J., Karns, T. K. B. & Ciereszko, L. S. (1976). *Acta Cryst.* B**32**, 1558–1560.

Weinheimer, A. J., Chang, C. W. J. & Matson, J. A. (1979). *Progress in the Chemistry of Organic Natural Products*, edited by W. Herz, H. Grisebach & G. W. Kirby, pp. 285–387. New York: Springer-Verlag.

Weinheimer, A. J., Middlebrook, R. E., Bledsoe, J. O. Jr, Marsico, W. E. & Karns, T. K. B. (1968). *Chem. Commun.* pp. 384–385.

Acta Cryst. (1996). C**52**, 1274-1277

(1*R*,2*S*,4*R*)-2-Benzyloxy-4-methoxy-5-(1-methylethyl)-6,8-dioxabicyclo[3.2.1]octane and (1*R*,2*S*,4*R*)-2-Benzyloxy-4-methoxy-2-methyl-6,8-dioxabicyclo[3.2.1]octane

GRAEME J. GAINSFORD, PETER C. TYLER AND RICHARD H. FURNEAUX

The New Zealand Institute for Industrial Research and Development, PO Box 31-310, Lower Hutt, New Zealand. E-mail: g.gainsford@irl.cri.nz

(*Received 6 September 1995; accepted 27 November 1995*)

Abstract

The title compounds, $C_{17}H_{24}O_4$ and $C_{15}H_{20}O_4$, respectively, were obtained during studies of the relationship between structure and herbicidal activity of derivatives of levoglucosenone [Furneax *et al.* (1989). European Patent Application 0 302 599; Furneaux, Henzell & Tyler (1991). US Patent 5 047 518; Blattner, Furneaux, Mason & Tyler (1991). *Pestic. Sci.* **31**, 419–435; Furneaux, Mason & Tyler (1995). Unpublished results]. The crystal structures contain independent molecules held together by van der Waals packing forces. The pendant groups at C1 in $C_{17}H_{24}O_4$ have a minor effect on the fused dioxolane–pyranose ring conformation. The *O*-benzyl groups adopt different conformations determined by minimization of intramolecular repulsive contacts, particularly for the 4-*C*-methyl molecule, and intermolecular non-bonding contacts.

Comment

Crystals of (1*R*,2*S*,4*R*)-2-benzyloxy-4-methoxy-5-(1-methylethyl)-6,8-dioxabicyclo[3.2.1]octane, (1), and (1*R*,2*S*,4*R*)-2-benzyloxy-4-methoxy-2-methyl-6,8-dioxabicyclo[3.2.1]octane, (2), with common name 1,6-anhydro-4-*O*-benzyl-3-deoxy-4-*C*-methyl-2-*O*-methyl-β-D-*ribo*-hexopyranose, were prepared, as noted by Furneaux, Henzell & Tyler (1991), during studies of structure–activity relationships of potent herbicides based on 1,6-anhydro-4-*O*-benzyl-3-deoxy-2-*O*-methyl-