riding on the bonded atom with their U_{iso} fixed at $1.2U_{eq}$ of the attached atom. All other H atoms were calculated to fit the geometry and their isotropic displacement parameters constrained to be the same and refined to 0.028 Å^2. The absolute configuration of the molecule was not determined since it was known from the synthesis and was assigned according to the configurational angles given by Cano *et al.* (1985). Calculation of the Flack absolute structure parameter χ and its e.s.d. [−0.2 (4); Flack, 1983] further suggests that the refined absolute structure is correct.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1991) and *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Clerodane Diterpene with Antibacterial Activity from *Ajuga lupulina*

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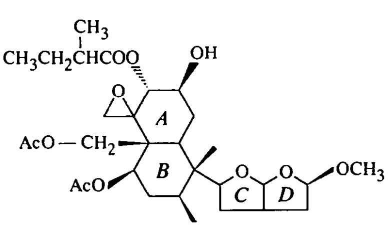
Abstract

The structure of a new diterpene, $C_{30}H_{46}O_{11}$, with antibacterial activity against *Pseudomonas aeruginose* and *Escherichia coli*, isolated from the fresh whole plants of *Ajuga lupulina* (Labiatae) was established to be 2β-hydroxy-2-methylbutanoyl-3α-lupulin (3-deoxy-14,15-dihydro-2-hydroxy-15-methoxy-caryoptinol 2-methylbutanoate), by means of X-ray crystallographic analysis. The present study confirms that the two six-membered rings are in ideal chair conformations.

Comment

As part of our ongoing research on diterpenoid compounds with antibacterial activity from *Ajuga lupulina* (Labiatae), a new clerodane diterpene, (I), with potential antibacterial activity against *Pseudomonas aeruginose* and *Escherichia coli*, was isolated from the fresh whole plants of *Ajuga lupulina*. In order to establish its structure, the X-ray analysis was undertaken. The results of the present study are in agreement with the structural elucidation based on spectroscopic data.



(I)

In rings *A* and *B*, the mean values of the valence angles (109.8 and 111.6°) are close to that of 111.6° for the chair form of cyclohexane obtained by Hendrickson (1967) from strain-energy minimization calculations. Rings *C* and *D* of the tetrahydrofurofuran ring exhibited envelope and planar conformations, respectively. The bond lengths of rings *C* and *D* vary from 1.397 (2) to 1.546 (2) Å. The mean values of bond lengths and valence angles are close to those of the tetrahydrofuran ring (Shiro & Koyama, 1970; Chen, Tan, Liu, Lie & Chen, 1996). The stereochemistry of the title compound was established by comparison with the absolute configuration of ajugareptansin (Solans, Miravitlles, Declercq & Germain, 1979), clerodin (Kato, Munakata & Katayama, 1973; Rogers *et al.*, 1979) and ajugarins IV and V (Kubo, Kido & Fukuyama, 1980; Kubo, Klocke, Miura & Fukuyama, 1982; Chen *et al.*, 1996) (Fig. 1). Owing to the unfavorable value of the reflection-to-parameter ratio (2310/380 = 6.08), the numerical values of the bond distances and angles must be taken with caution.

The structure is stabilized by intermolecular hydrogen bonds between the O(4) and O(9^i) atoms [O(4)—H(4*A*) 0.85, H(4*A*)···O(9^i) 2.04 Å and O(4)—H(4*A*)···O(9^i) 178.6°; symmetry code: (i) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $2-z$]. Due to disorder, the U^{ij} and U_{eq} values for the C(29) and C(30) atoms are large. The C(30) atom [site occupancy factors (s.o.f.) for C(30) and C(30′) were fixed at 0.6 and 0.4, respectively] is found to be highly disordered.

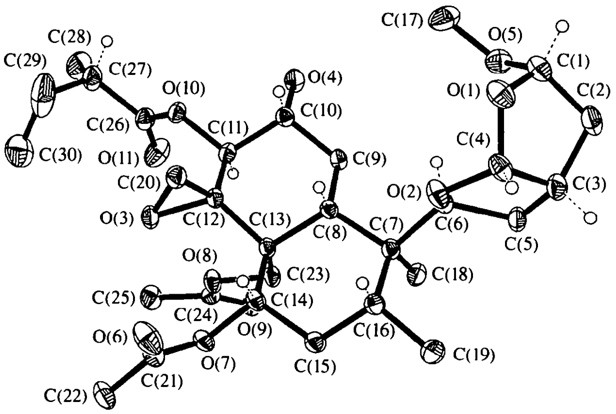


Fig. 1. View of the title molecule with the atom-numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are at the 30% probability level.

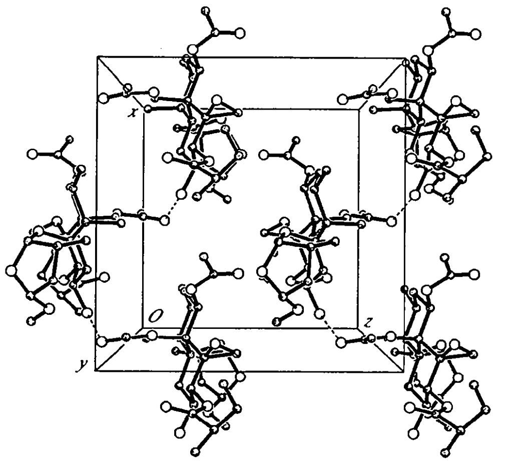


Fig. 2. Crystal-packing diagram of the title compound.

Experimental

The title compound (m.p. 445–447 K) was isolated from the fresh whole plant of *Ajuga lupulina*. After purification by preparative TLC, a single crystal was obtained from *n*-hexane–EtOAc (2:1).

Crystal data

$C_{30}H_{46}O_{11}$
$M_r = 582.7$
Orthorhombic
$P2_12_12_1$
$a = 10.750\,(2)$ Å
$b = 26.735\,(6)$ Å
$c = 10.533\,(1)$ Å
$V = 3027.2\,(15)$ Å^3
$Z = 4$
$D_x = 1.278$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 18.71$–$21.39°$
$\mu = 0.097$ mm^{-1}
$T = 293$ K
Prism
0.30 × 0.20 × 0.20 mm
Colorless

Data collection

Rigaku AFC-7*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2995 measured reflections
2945 independent reflections
2310 reflections with $F > 4\sigma(F)$

$R_{\rm int} = 0.004$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 31$
$l = 0 \rightarrow 12$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on *F*
$R = 0.0465$
$wR = 0.0614$
$S = 2.38$
2310 reflections
380 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{\rm max} = 0.020$

$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.41$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: $4\,(4) \times 10^{-4}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O(1)—C(1)	1.415 (1)	O(6)—C(21)	1.188 (1)
O(3)—C(12)	1.429 (2)	C(8)—C(13)	1.593 (2)
O(3)—C(20)	1.453 (2)	C(12)—C(20)	1.480 (1)
O(4)—C(10)	1.426 (1)	C(13)—C(14)	1.531 (1)
O(5)—C(17)	1.427 (2)	C(13)—C(23)	1.538 (1)
C(12)—O(3)—C(20)	61.8 (1)	C(6)—C(7)—C(8)	107.1 (1)
C(1)—O(5)—C(17)	114.7 (1)	O(4)—C(10)—C(9)	112.0 (1)
O(5)—C(1)—C(2)	108.8 (1)	O(3)—C(12)—C(11)	115.6 (1)
C(2)—C(3)—C(4)	103.7 (1)	O(3)—C(12)—C(20)	59.9 (1)
C(2)—C(3)—C(5)	116.6 (1)	C(13)—C(12)—C(20)	122.6 (1)
O(1)—C(4)—O(2)	112.9 (1)	C(8)—C(13)—C(12)	103.8 (1)
O(2)—C(4)—C(3)	108.4 (1)	C(12)—C(13)—C(23)	109.2 (1)
O(2)—C(6)—C(7)	110.5 (1)	O(6)—C(21)—O(7)	124.2 (2)

For data collection, a scan width of (1.00 + 0.30tanθ)° (in ω) and a scan speed of 16.0° min^{-1} were used. A colorless prism crystal was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1985) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically by full-matrix least squares. H atoms were placed in calculated positions (C—H 0.96 Å), assigned fixed isotropic displacement parameters and allowed to ride on their respective parent atoms. The contributions of these H atoms were included in the structure-factor calculations. The C(29) H atoms [s.o.f.'s for H(29*B*) and H(29*C*) were fixed at 0.6 and 0.4, respectively], and the C(30) and C(30′) H atoms [s.o.f.'s for atoms H(30*A*)–H(30*C*) and H(30*D*)–H(30*F*) were fixed at 0.6 and 0.4, respectively] were found to be highly disordered. Neutral atom scattering factors were taken from Cromer & Waber (1974). Anomalous dispersion effects were included in F_{calc} (Ibers & Hamilton, 1964). The values for the mass attenuation coefficients are those of Creagh & Hubbel (1992). All calculations were performed on a PC586 using the *SHELXTL-Plus* (Sheldrick, 1991) program package.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,6,10,12-Tetraphenyl-7,9-dioxa-1,3-dithiacyclododecane

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Abstract

The title compound, $C_{32}H_{32}O_2S_2$, is a mixed oxa–thia crown macrocycle. The molecule has all heteroatoms at side positions of a quadrangular skeleton. Both sulfur and oxygen conformational arrangements are virtually the same.

Comment

Sulfur coronands possess solid-state conformations that differ significantly from those of their oxygen counterparts and yield metal complexes with unexpected reactivity and redox properties (Cooper, 1988). In this context, we have isolated the title compound, (I), which, in addition to its potential as a transition metal complexing agent, is an interesting candidate for conformational studies since it contains both S and O heteroatoms in a novel arrangement.

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