N93—N92—C961	118.8 (5)	C961—C971—C981	115.2 (9)
N93—N92—C962	119.6 (7)	N92—C962—C992	114 (2)
N92—N93—C94	103.8 (4)	N92—C962—C972	108 (1)
N90—C94—N93	112.8 (4)	C972—C962—C992	106 (2)
N92—C961—C991	114.6 (7)	C962—C972—C982	112 (2)
N2—N1—C6—C7	−88.5 (6)	N52—N51—C56—C57	91.8 (6)
N1—C6—C7—O8	65.2 (5)	N51—C56—C57—O58	−61.3 (6)
N1—C6—C7—O11	−51.6 (5)	N51—C56—C57—O61	54.2 (6)
N1—C6—C7—C12	−174.6 (4)	N51—C56—C57—C62	178.5 (4)
C6—C7—C12—C13	80.3 (6)	C56—C57—C62—C63	−83.1 (6)
O8—C9—C20—O21	64.0 (5)	O58—C59—C70—O71	−60.9 (6)
C9—C20—O21—C22	−171.7 (4)	C59—C70—O71—C72	172.2 (5)
C20—O21—C22—C27	102.7 (6)	C70—O71—C72—C77	8.8 (8)
C36—C37—N40—C41	158.5 (6)	C86—C87—N90—C91	−133.9 (6)

The *sec*-butyl moieties are statistically disordered. Both *R* and *S* configurations are present at the same location and were refined isotropically with geometric restraints. The sum of the occupancy factors was constrained to 1. The refined occupancy factors for atoms C461–C491 and C961–C991 are 0.43 (1) and 0.68 (1), respectively.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*2.1 (McArdle, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

The authors thank Dr J. Tollenaere of Janssen Research Foundation (Beerse, Belgium) for providing a sample of the title compound.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1232). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2229–2231

Lupulin D

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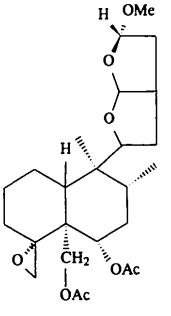
(*Received 26 October 1995; accepted 11 April 1996*)

Abstract

In the title compound, 3-deoxy-14,15-dihydro-15-methoxycaryoptinol, $C_{25}H_{38}O_8$, the conformation of the 15-methoxy group has been determined by X-ray analysis. The structure is stabilized by van der Waals interactions.

Comment

Most clerodane diterpenes from *Clerodandron* and *Ajuga* plants possess insect antifeedant activity (Camps & Coll, 1993). Extensive research indicates that the antifeedant activity of clerodane diterpenes may be related to a synergistic action of the furanofuran ring and the epoxy diacetate groups of the *trans*-decalin moiety (Belles, Camps, Coll & Piulachs, 1985). Recently, we obtained lupulin D, a clerodane diterpene from the whole plants of *Ajuga lupulina* Maxim, in crystal form. This compound, first isolated from the leaves of *Clerodandron brachyanthum* by Lin, Kuo & Chen (1989), was the first reported clerodane diterpene with a methoxy group at C17. Its structure was established by spectral methods and chemical correlation; however, the determination of the conformation of the methoxy group at C17 was difficult. Lin *et al.* (1989) presumed that the methoxy group at C17 has an α orientation. In order to confirm this presumption, the X-ray analysis was undertaken. The two six-membered rings of the *trans*-fused decalin ring system are in normal chair conformations while the furan rings of the *cis*-fused hexahydrofuranofuran system are in envelope conformations. The re-



Lupulin D

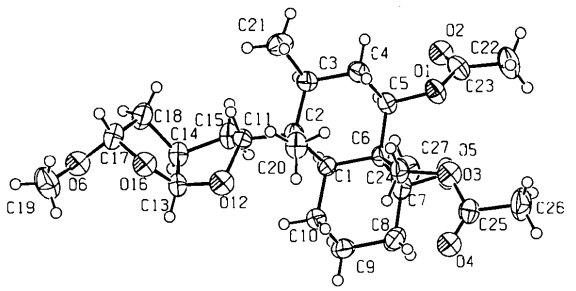


Fig. 1. View of the title molecule with the atom-numbering scheme for the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

sults of the present analysis are in agreement with the structural elucidation of Lin *et al.* (1989). The structure is stabilized by van der Waals interactions.

Experimental

Crystals of lupulin D were obtained from a petroleum ether–ethyl ether–MeOH (1:1:1) extract of the whole plants of *Ajuga lupulina* after purification by chromatography on silica gel. The single crystal was obtained from *n*-hexane–Me_2CO (3:1).

Crystal data

$C_{25}H_{38}O_8$
M_r = 466.6
Orthorhombic
$P2_12_12_1$
a = 10.114 (3) Å
b = 11.289 (4) Å
c = 21.103 (9) Å
V = 2409 (2) Å^3
Z = 4
D_x = 1.29 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–13°
μ = 0.887 mm^{-1}
T = 293 (1) K
Block
0.50 × 0.45 × 0.30 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.93, T_{max} = 1.00
2436 measured reflections
2436 independent reflections
2058 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 25°
h = 0 → 12
k = 0 → 13
l = 0 → 25
3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F
R = 0.039
wR = 0.037
S = 0.841
2058 reflections
299 parameters
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.212 e Å^{-3}
$\Delta\rho_{min}$ = 0.000 e Å^{-3}
Extinction correction: $|F_c|/(1+gI_c)$
Extinction coefficient: g = 4 × 10^{-7}
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)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O1	0.8469 (2)	0.3821 (2)	0.8588 (1)	3.31 (5)
O2	0.8914 (4)	0.4707 (2)	0.9509 (1)	6.11 (7)
O3	0.6641 (2)	0.2629 (2)	0.7881 (1)	3.72 (5)
O4	0.5289 (3)	0.1385 (2)	0.7367 (1)	4.41 (6)
O5	0.6305 (3)	0.2831 (2)	0.9266 (1)	4.97 (6)
O6	1.3417 (3)	−0.4239 (2)	0.9422 (1)	4.30 (6)
O12	1.0521 (2)	−0.1854 (2)	0.8623 (1)	3.80 (5)
O16	1.2363 (3)	−0.3068 (2)	0.8671 (1)	4.38 (5)
C1	0.8861 (3)	0.0504 (3)	0.8823 (1)	2.44 (6)
C2	1.0252 (3)	0.0330 (3)	0.8506 (1)	2.62 (6)
C3	1.1094 (3)	0.1453 (3)	0.8640 (2)	3.09 (7)
C4	1.0371 (4)	0.2587 (3)	0.8451 (2)	3.40 (7)
C5	0.9063 (3)	0.2716 (3)	0.8792 (2)	2.81 (6)
C6	0.8108 (3)	0.1696 (3)	0.8662 (1)	2.52 (6)
C7	0.6903 (3)	0.1698 (3)	0.9112 (2)	3.17 (7)
C8	0.5949 (3)	0.0695 (3)	0.9017 (2)	3.75 (7)
C9	0.6686 (3)	−0.0464 (3)	0.9146 (2)	3.76 (8)
C10	0.7940 (3)	−0.0577 (3)	0.8754 (2)	3.29 (7)
C11	1.1028 (3)	−0.0710 (3)	0.8804 (1)	2.73 (6)
C13	1.1196 (4)	−0.2692 (3)	0.8996 (2)	3.72 (7)
C14	1.1662 (4)	−0.2069 (3)	0.9606 (2)	3.29 (7)
C15	1.1144 (4)	−0.0799 (3)	0.9521 (2)	3.28 (7)
C17	1.3417 (4)	−0.3153 (3)	0.9103 (2)	3.58 (7)
C18	1.3176 (4)	−0.2178 (3)	0.9584 (2)	4.21 (8)
C19	1.3681 (5)	−0.5224 (4)	0.9021 (2)	6.0 (1)
C20	1.0171 (4)	0.0063 (3)	0.7784 (2)	3.59 (7)
C21	1.2476 (4)	0.1466 (4)	0.8338 (2)	5.6 (1)
C22	0.8416 (4)	0.4721 (3)	0.8992 (2)	3.73 (8)
C23	0.7658 (5)	0.5741 (3)	0.8724 (2)	5.1 (1)
C24	0.7627 (3)	0.1720 (3)	0.7968 (2)	3.21 (7)
C25	0.5574 (4)	0.2357 (3)	0.7543 (2)	3.38 (7)
C26	0.4792 (4)	0.3461 (2)	0.7401 (2)	5.6 (1)
C27	0.6981 (4)	0.2178 (4)	0.9757 (2)	4.54 (9)

Table 2. *Selected geometric parameters (Å, °)*

O6—C17	1.398 (5)	O16—C17	1.407 (5)
O6—C19	1.422 (5)	C17—C18	1.517 (6)
C17—O6—C19	113.5 (3)	O6—C17—C18	108.3 (3)
C13—O16—C17	109.6 (3)	O16—C17—C18	105.2 (3)
O6—C17—O16	111.8 (4)	C14—C18—C17	103.8 (4)

All H-atom positions were calculated geometrically and included in the structural-factor calculations as riding atoms with isotropic displacement parameters 1.3 times that of the attached atom. All calculations were performed on a MicroVAXII using *SDP* (Frenz, 1978).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP*/VAX (Frenz, 1978). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *LSFM* (*SDP*/*VAX*). Molecular graphics: *ORTEP* (Johnson, 1965), *SDP*/VAX. Software used to prepare material for publication: *SDP*/VAX.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2231–2236

Substituted Imidazonaphthyridine Derivatives. I. $C_{19}H_{14}F_3N_3$, $C_{18}H_{10}F_5N_3$, $C_{18}H_{11}ClF_3N_3$ and $C_{18}H_{11}BrF_3N_3$

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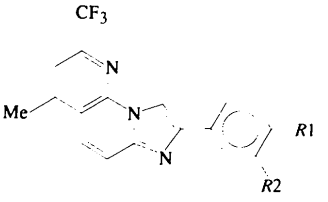
(*Received 5 December 1995; accepted 14 March 1996*)

Abstract

The structures of four 2,6,8-trisubstituted imidazonaphthyridine derivatives, 6-methyl-2-(4-methylphenyl)-8-trifluoromethylimidazo[1,2-*a*][1,8]naphthyridine, (I), 2-(3,4-difluorophenyl)-6-methyl-8-trifluoromethylimidazo-[1,2-*a*][1,8]naphthyridine, (II), 2-(4-chlorophenyl)-6-methyl-8-trifluoromethylimidazo[1,2-*a*][1,8]naphthyridine, (III), and 2-(4-bromophenyl)-6-methyl-8-trifluoromethylimidazo[1,2-*a*][1,8]naphthyridine, (IV), are reported. The molecules are planar and exist as dimers, formed through intermolecular C—H···N hydrogen bonds in all four cases. The trifluoromethyl group undergoes rotational disorder in (II)–(IV). The molecules are laid in two-dimensional planes in the crystal lattice with possible intermoleculear π–π interactions.

Comment

Imidazo[1,2-*a*]pyridine derivatives have been found to have potential biological activities and photophysical properties (Kaminski *et al.*, 1989; Knolker & Boese, 1988). Recently, imidazo[1,2-*a*]1,8-naphthyridine derivatives were reported to possess potential antibacterial activity (Kondo, Taguchi, Inoue, Sakamoto & Tsukamoto, 1990). This prompted us to synthesize a series of imidazonaphthyridine compounds, characterize them, and study their biological and photophysical properties. Like their pyridine analogues, these compounds also show fluorescence in the visible region. We have obtained the compounds *via* facile condensation of 2-amino-1,8-naphthyridine with appropriate 1,3-dicarbonyl compounds (Chua & Jackson, 1995; Anwair, 1995). Although 1- and 2-substituted isomers are possible, only the 2-substituted isomer has been isolated consistently. We have determined the crystal structures and hereby report the structures of four of them. We believe that this is the first report on the crystal structures of imidazonaphthyridines. Compounds (III) and (IV) are isomorphous.



	*R*1	*R*2
(I)	Me	H
(II)	F	F
(III)	Cl	H
(IV)	Br	H

All four structures confirm the double bonds N1=C1, C2=C3 and C9=C10 and the other bond lengths and angles are normal. The imidazonaphthyridine moiety is planar in each case, with maximum deviations of 0.044 (2) (C5), 0.036 (5) (C5), 0.024 (2) (C5) and 0.023 (6) Å (C6), and dihedral angles between the planes of the imidazonaphthyridine moiety and the phenyl ring of 6.6 (1), 1.5 (1), 6.9 (1) and 7.8 (1)° in (I), (II), (III) and (IV), respectively. Hence each molecule is almost planar.

All four compounds crystallize in the triclinic space group $P\bar{1}$ and form dimeric pairs through intermolecular C2—H2···N1 hydrogen bonds around the inversion centres. The C2···N1 distance is found to increase with heavier halogen substitution at C14 (in the order F, Cl, Br). The halogen atoms in (II), (III) and (IV) have interactions with the F atoms of the trifluoromethyl group

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