Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Pseudokobusine

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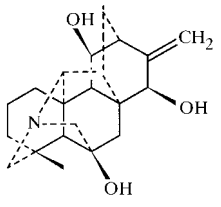
Received 27 June 2000
Accepted 19 September 2000

The title compound, hetisan-6,11β,15β-triol, $C_{20}H_{27}NO_3$, is a hetisane-type diterpenoid alkaloid. It consists of six six-membered rings and two five-membered rings. The fused-ring system contains three chair, two boat, one distorted boat and two envelope conformations. Intramolecular and intermolecular hydrogen bonds are present between the O atoms, with O$\cdots$O separations of 3.006 (3) and 2.743 (3) Å, as well as an O$\cdots$N intermolecular interaction of 2.887 (3) Å.

Comment

Investigations on the alkaloid constituents of the roots of *Aconitum nasutum* obtained from Trabzon-Sürmene, Arpali, Turkey, led to the isolation of the title compound, (I). Aconite root and alkaloids of this plant have been used for thousands of years in Eurasia as a powerful toxin, an arrow poison and a drug. Since ancient times, the Chinese have processed aconite roots to decrease its toxicity for safe usage in the treatment of weak constitution, poor metabolism, dysuria, cardiac weakness, gout, rheumatism, neuralgia and chill, while Western medicine utilizes it for chronic rheumatism and neuralgia (Saito *et al.*, 1982).



(I)

The molecular structure of (I) (Fig. 1) contains an alkenyl $=CH_2$ group attached at C16 with a C$=$C distance of 1.303 (4) Å. It has a masked amino alcohol group (N—C—OH) which is generally stable to oxidation and reduction (Natsume, 1962). Considering the three hydroxyl groups of the molecule, the tertiary hydroxyl at C6 forms a masked amino alcohol with the tertiary N1 atom and one of the two secondary hydroxyl groups is beside the allyl alcohol functional group. There was an ambiguity in the location of the remaining hydroxyl group. Two alternate structures were attributed to pseudokobusine, based on the two positions of the third hydroxyl group at either C11 or at C12 (Natsume, 1962). The X-ray structure analysis has established the former structure, with the hydroxyl group at C11.

The value of the Flack (1983) parameter obtained, −0.5 (16), is inadequate to indicate the absolute configuration. The absolute stereochemistry has been established by convention (Okamoto *et al.*, 1962) and hence the present enantiomer has been retained. There are chiral centres in the present structure and the respective configurations are 4*R*, 5*R*, 6*R*, 8*R*, 9*S*, 10*S*, 11*R*, 12*R*, 14*S*, 15*S* and 20*R*.

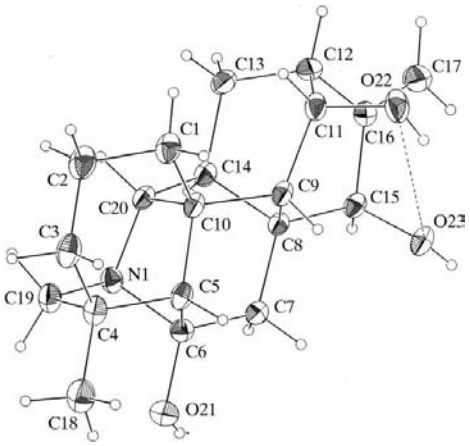


Figure 1
The structure of (I) with 30% probability displacement ellipsoids and the atom-numbering scheme.

The molecule is composed of eight fused rings, six of which are six-membered and two of which are five-membered. Rings *A* (C1–C5/C10), *B* (C5–C9/C10) and *D* (C6–C8/C14/C20/N1) adopt the chair conformation (Table 2), ring *C* (C8/C9/C11/C12/C16/C15) is in a distorted boat conformation, ring *E* (C8/C12–C16) is in a boat conformation, while ring *F* (N1/C19/C4/C5/C10/C20) is in a distorted boat conformation. The two five-membered rings, *G* (C4–C6/N1/C19) and *H* (C8–C10/C14/C20), adopt an envelope conformation with the apex at C6 and C8, respectively. The O21 atom of the hydroxyl group at C6 is equatorial to ring *B* and the associated torsion angles are −174.7 (2) (C10—C5—C6—O21) and −179.2 (2)° (O21—C6—C7—C8). The hydroxyl group at C11 is twisted from the plane of ring *C*, with torsion angles of −105.6 (3) (C8—C9—C11—O22) and 55.9 (3)° (O22—C11—C12—C16). The alkenyl group at C16 is equatorial to ring *C*, with torsion angles of −129.2 (3) (C11—C12—C16—C17) and −168.4 (3)° (C8—C15—C16—C17). The hydroxyl group at C15 is twisted from the plane of ring *C*, the torsion angles being −105.4 (3) (O23—C15—C16—C12) and 56.6 (3)° (C9—C8—C15—O23). The ring-puckering parameters (Table 2) were calculated using the method of Cremer & Pople (1975). The Csp^3—N bond lengths range between 1.486 (4) and 1.513 (3) Å. The Csp^3—O bond lengths range from 1.403 (3) to 1.448 (3) Å.

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The O21 hydroxyl group at C16 forms an intermolecular O—H···O hydrogen bond with the O22 hydroxyl group bonded to C11 [O21···O22^{i} 2.743 (3) Å; symmetry code: (i) $x+1, y, z$], and an intramolecular hydrogen bond is formed by O22 with the O23 hydroxyl group at C15 [O22···O23 3.006 (3) Å]. An O—H···N hydrogen bond completes the intermolecular interactions [O23···N1^{ii} 2.887 (3) Å; symmetry code: (ii) $1-x, \frac{1}{2}+y, -z$]. In kobusine methiodide, the contact distance between the two O atoms of the two hydroxyl groups at the same position as in the present molecule was calculated to be 2.81 Å, indicating a strong intermolecular hydrogen bond (Pelletier *et al.*, 1970).

Experimental

The crude alkaloid extract obtained from the roots of *Aconitum nasutum* was first separated by vacuum liquid chromatography (VLC) on basic Al_2O_3 and eluted with $CHCl_3$/MeOH mixtures. VLC fractions 32–36 ($CHCl_3$/MeOH 90:1) (942 mg) were separated on a basic Al_2O_3 rotor with hexane/chloroform/methanol mixtures and pseudokobusine was subsequently isolated. Crystals of the title compound were obtained from a solution of the compound in methanol by slow evaporation at room temperature.

Crystal data

$C_{20}H_{27}NO_3$
$M_r = 329.43$
Monoclinic, $P2_1$
$a = 8.0746$ (8) Å
$b = 11.4613$ (11) Å
$c = 9.1121$ (9) Å
$\beta = 90.338$ (2)°
$V = 843.27$ (14) Å^3
$Z = 2$
$D_x = 1.297$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6766 reflections
$\theta = 3.00$–$30.55°$
$\mu = 0.086$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.38 × 0.26 × 0.19 mm

Data collection

Bruker 1000 diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1998)
$T_{min} = 0.97$, $T_{max} = 0.98$
6766 measured reflections
2455 independent reflections
1335 reflections with $I > 2\sigma(I)$
$R_{int} = 0.05$
$\theta_{max} = 30.55°$
$h = -11 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -12 \rightarrow 12$
Intensity decay: negligible

Table 1
Selected geometric parameters (Å, °).

C6—O21	1.403 (3)	C14—C20	1.522 (4)
C11—O22	1.440 (3)	C16—C17	1.303 (4)
C15—O23	1.448 (3)	C19—N1	1.488 (4)
C6—N1	1.513 (3)	C20—N1	1.486 (4)
O21—C6—C5	111.9 (2)	C17—C16—C15	123.5 (3)
O21—C6—C7	110.9 (2)	C19—N1—C20	108.2 (2)
N1—C6—C7	111.4 (2)	C19—N1—C6	101.6 (2)
C17—C16—C12	124.5 (3)	C20—N1—C6	99.2 (2)
C10—C5—C6—O21	−174.7 (2)	C9—C8—C15—O23	56.6 (3)
O21—C6—C7—C8	−179.2 (2)	C11—C12—C16—C17	−129.2 (3)
C8—C9—C11—O22	−105.6 (3)	O23—C15—C16—C12	−105.4 (3)
O22—C11—C12—C16	55.9 (3)	C8—C15—C16—C17	−168.4 (3)

Table 2
Ring-puckering parameters (Å,°) for eight rings.

Ring	q_2	q_3	Q_T	θ
A	0.014 (3)	−0.517 (3)	0.518 (3)	178.5 (3)
B	0.205 (2)	−0.655 (2)	0.686 (2)	162.7 (2)
C	0.805 (3)	0.021 (3)	0.805 (3)	88.5 (2)
D	0.149 (3)	−0.668 (3)	0.684 (3)	167.4 (2)
E	0.788 (3)	−0.051 (3)	0.789 (3)	93.7 (2)
F	0.929 (3)	−0.022 (3)	0.929 (3)	91.4 (2)
G	0.557 (3)			
H	0.549 (3)			

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.094$
$S = 0.813$
2455 reflections
222 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0430P)^2 + 0.0279P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.006 (2)

The methyl H atoms on C18 and C19 and the hydroxyl H atoms attached to O21, O22 and O23 were allowed to ride on their parent atoms with $U_{iso} = 1.5U_{eq}$. The remaining H atoms were included at geometrically calculated positions and allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}$(parent).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SHELXTLNT* (Bruker, 1999); program(s) used to solve structure: *SIR*97 (Cascarano *et al.*, 1996); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1019). Services for accessing these data are described at the back of the journal.

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ISSN 0108-2701

Pseudokobusine. Erratum

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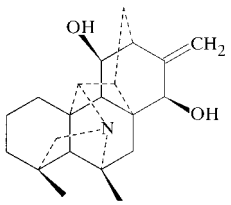
In the paper by Bhattacharyya *et al.* [*Acta Cryst*. (2001), C**57**, 68–69], the chemical diagram of the title compound, $C_{20}H_{27}NO_3$, is incorrect.

Comment

When comparing the revised diagram of pseudokobusine, (I), with the *ORTEP* drawing (Fig. 1), the N1 atom is connected to



(I)

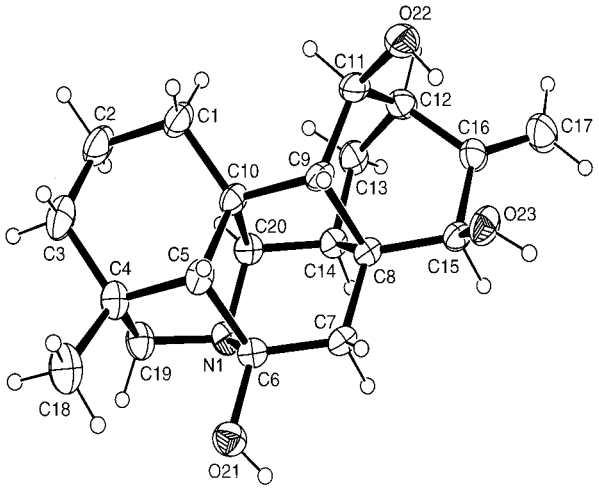


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids and the atom-numbering scheme.

the C6 atom of the hydroxyl group, but in the diagram published originally, the N1 atom is not connected to a C atom bearing a hydroxyl group. The molecular formula of the erroneous structure would be $C_{21}H_{29}NO_3$ and not $C_{20}H_{27}NO_3$, as it should be.

References

Bhattacharyya, K., Kar, T., Bocelli, G., Righi, L. & Joshi, B. S. (2001). *Acta Cryst.* C**57**, 68–69.