

number of scans was varied to maintain constant $\sigma(F)/F = 0.017$ with a maximum of eight scans; ω -scan rate 8° min^{-1} with ω -scan width $(0.787 + 0.3 \tan \theta)^\circ$. The crystal chosen for experiment was found to be a twin crystal, where the $hk0$ reflections from the two crystal halves overlap each other. The data were collected for the halves as separate subsets. A value of R_{int} is missing since in each subset only a unique data set was collected. The data files were merged without averaging. From the diffraction symmetry the space groups $P1$ and $\bar{P}1$ were possible. The structure was solved and refined in $P1$; lowering the symmetry to $P1$ gave no significant improvement in the R factors. The As and S atoms were found in a Patterson synthesis; the rest of the structure (except for H atoms) was found in successive Fourier syntheses. All H-atom positions were first calculated geometrically, using a C—H distance of 1.08 Å. These positions were subsequently refined without constraints. The C-ring H atoms were restricted to have identical isotropic displacement parameters. Similarly, the displacement parameters of the H atoms in each —CH₃ group were kept the same. The two subsets were given different scale factors in the refinement. For the $hk0$ reflections two other scale factors were introduced, making in total four different scale factors to be used in the refinements. After the final refinement all H-atom positions were recalculated (C—H 1.08 Å). In the geometrical calculations (*cf.* Table 3) e.s.d.'s for the H-atom positions were taken from the refinement. The molecular plots were made using ORTEPII (Johnson, 1976). Other calculations were made using the TEXSAN program system (Molecular Structure Corporation, 1989).

This work has been supported by a grant from the National Swedish Board for Technical Development, which is hereby gratefully acknowledged. The authors also wish to thank Dr Jonas Hellberg for providing the crystals and Hilding Karlsson for expert technical advice during the data collection.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55473 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1022]

References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Molecular Structure Corporation (1989). TEXSAN. TEXRAY Structure Analysis Package. Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77391, USA.
 Noreland, J., Olovsson, G. & Olovsson, I. (1992). *Acta Cryst.* **C48**, 1459–1462.
 Olovsson, G. & Olovsson, I. (1991). *Acta Cryst.* **B47**, 355–362.
 Olovsson, G. & Olovsson, I. (1992a). In preparation.
 Olovsson, G. & Olovsson, I. (1992b). *Acta Cryst.* Submitted.

Acta Cryst. (1993). **C49**, 171–173

Structure of Kopsine: Methyl 3-Hydroxy-22-oxokopsan-1-carboxylate

WILLIAM WATT

Research Laboratories, The Upjohn Company, Kalamazoo, MI 49007, USA

RATNA GHOSH

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

TAPAN SEAL AND BISWAPATI MUKHERJEE

Department of Pharmacology, B. C. Roy Postgraduate Institute of Basic Medical Sciences, 244B A. J. C. Bose Road, Calcutta 700 020, India

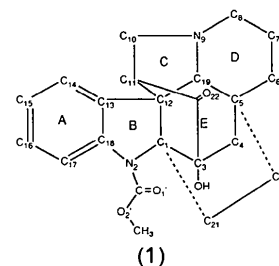
(Received 30 July 1992; accepted 24 September 1992)

Abstract

The Kopsine molecule consists of five fused rings. The phenyl ring *A* is almost planar. The conformation of ring *B* is a pure envelope, ring *C* is a half-chair, ring *D* is a chair and ring *E* is a boat. An intramolecular hydrogen bond $\text{O}(3) \cdots \text{H}(\text{O}3) \cdots \text{O}(1')$ helps to stabilize the boat conformation of ring *E*.

Comment

Kopsine, $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_4$, m.p. 487–489 K, was isolated from the leaves of *Kopsia fruticosa*. The structure of Kopsine (1) with its absolute configuration was previously deduced by Guggisberg, Gorman, Bycroft & Schmid (1969) through the application of physical methods, mainly NMR. The complete structure of Kopsine with relative configuration and various ring conformations has been established by X-ray crystallography.



The isolation was carried out as follows: air dried and coarsely powdered leaves (750 g) of *Kopsia fruticosa* (identified by Dr S. R. Das, Plant Survey Officer, CCRAS, Calcutta, and a specimen preserved in the laboratory) were extracted with petroleum ether (b.p. 333–353 K) in a soxhlet apparatus for 18 h. The concentrated

extract was churned with citric acid (5%, 2×250 ml). The combined extract was washed with petroleum ether (b.p. 313–333 K) (2×100 ml). The citric acid was basified (pH 10) with cold NH₄OH and the free base was extracted with benzene (3×100 ml). After washing, (3×50 ml), then drying (Na₂SO₄), the benzene extract was concentrated (50 ml) and allowed to stand overnight. Large, chunky crystals (800 mg) appeared and were then recrystallized from ethyl acetate/acetone.

The analysis of this structure has established the relative configuration of Kopsine. This compound has the same skeleton as the *Aspidosperma* alkaloids, first established conclusively by X-ray analysis of (-)-aspidospermine N(b)-methiodide (Mills & Nyburg, 1960). This alkaloid has four asymmetric centers and the ring systems are designated in (1). The Kopsine molecule consists of five fused rings lettered A to E with the phenyl ring A being almost planar. A torsion angle of -1.2(4)° for C(12)—C(13)—C(18)—N(2) indicates that the atoms in the five-membered ring B are planar. The deviation of C(1) from this plane shows that ring B has a 'pure envelope' conformation (Ramakrishnan, 1980). The endocyclic torsion angles of ring D have slight deviations from the ideal value of 54° for a 'chair conformation' (Hendrickson, 1967). The conformation of ring C is a half-chair, and ring E is a boat, as is evident from the torsion angles (Ramakrishnan, 1980). Lengthening of the N(2)—C(1) and N(2)—C(18) bonds results from the strain arising from the chain O(1')—C(1')—O(2')—C(3'). The lengthening of C(8)—N(9) and N(9)—C(10) is due to overcrowding. The intramolecular hydrogen bond O(3)—H(O3)···O(1') [O(3)···O(1') 2.641(4), H(O3)···O(1') 1.96 Å, O(3)—H(O3)···O(1') 122°] helps to stabilize the boat conformation of ring E. The dihedral angles formed by the planes P(A), P(B), P(C), P(D) and P(E) have the following values: P(A)P(C) = 80.2°, P(A)P(D) = 39.6°, P(A)P(E) = 26.3°, P(C)P(D) = 62.4°, P(C)P(E) = 80.2° and P(D)P(E) = 53.9°. These values are in agreement with other alkaloids of the *Aspidosperma* type (Toffoli, Rodier, Lewin & Poisson, 1986; Camerman, Camerman & Trotter, 1965; Chiaroni, Langlois & Riche, 1977).

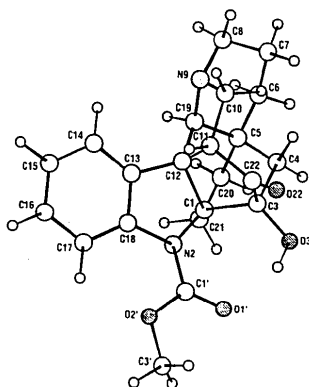


Fig. 1. View of C₂₂H₂₄N₂O₄ showing the labelling of the non-H atoms.

Experimental

Crystal data

C₂₂H₂₄N₂O₄
M_r = 380.43
 Orthorhombic
 P2₁2₁2₁
a = 10.193 (3) Å
b = 11.966 (1) Å
c = 14.802 (3) Å
V = 1805.4 (7) Å³
Z = 4
D_x = 1.40 Mg m⁻³

Cu Kα radiation
 λ = 1.5418 Å
 Cell parameters from 25 reflections
 θ = 60–68°
 μ = 0.699 mm⁻¹
T = 158 K
 Chunky block
 0.36 × 0.09 × 0.48 mm
 Clear

Data collection

Siemens P2₁ diffractometer
 θ/2θ scans
 1775 measured reflections
 1775 independent reflections
 1689 observed reflections
 [I > 3.0σ(I)]
 θ_{max} = 68°

h = -12 → 12
k = 0 → 14
l = -18 → 18
 10 standard reflections monitored every 200 reflections
 intensity variation: none

Refinement

Refinement on *F*²
 Final *R* = 0.045
wR = 0.122
 1772 reflections
 349 parameters
 H-atom parameters not refined
 Calculated weights *w* = 1/[σ²(*F*²)]
 (Δ/σ)_{max} = 0.020
 Δρ_{max} = 0.314 e Å⁻³

Δρ_{min} = -0.32 e Å⁻³
 Atomic scattering factors from Cromer & Liberman (1970) (C, N, O); *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1) (H)
 The absolute configuration was established by NMR (Guggisberg, Gorman, Bycroft & Schmid, 1969)

Cell refinement: performed using the program of Duchamp (1977). Data reduction: CRYM (Duchamp, 1984). Program(s) used to solve structure: MULTAN (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Program(s) used to refine structure: CRYM (Duchamp, 1984).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C(1)	-0.7144 (4)	-0.2750 (3)	-0.7167 (2)	1.3 (1)
N(2)	-0.8026 (3)	-0.2595 (2)	-0.7970 (2)	1.5 (1)
C(1')	-0.7707 (4)	-0.1927 (3)	-0.8683 (2)	2.0 (2)
O(1')	-0.6634 (3)	-0.1515 (2)	-0.8814 (2)	2.4 (1)
O(2')	-0.8718 (3)	-0.1789 (2)	-0.9256 (2)	2.0 (1)
C(3')	-0.8381 (4)	-0.1217 (4)	-1.0093 (2)	2.6 (2)
C(3)	-0.5729 (4)	-0.3196 (3)	-0.7328 (2)	1.8 (2)
O(3)	-0.4842 (3)	-0.2575 (2)	-0.7851 (2)	2.2 (1)
C(4)	-0.5120 (4)	-0.3311 (3)	-0.6351 (2)	1.8 (2)
C(5)	-0.6129 (4)	-0.3135 (3)	-0.5580 (2)	1.7 (2)
C(6)	-0.5527 (4)	-0.3416 (3)	-0.4655 (2)	2.0 (2)
C(7)	-0.5334 (4)	-0.4674 (3)	-0.4523 (2)	2.2 (2)
C(8)	-0.6643 (4)	-0.5289 (3)	-0.4669 (2)	2.1 (2)
N(9)	-0.7282 (3)	-0.5037 (2)	-0.5536 (2)	1.7 (1)
C(10)	-0.6677 (4)	-0.5581 (3)	-0.6325 (2)	1.8 (2)
C(11)	-0.7111 (4)	-0.4848 (3)	-0.7132 (2)	1.6 (2)
C(12)	-0.7783 (4)	-0.3786 (3)	-0.6710 (2)	1.4 (1)
C(13)	-0.9195 (4)	-0.3693 (3)	-0.6966 (2)	1.4 (1)
C(14)	-1.0250 (4)	-0.4225 (3)	-0.6591 (2)	1.6 (2)

C(15)	-1.1479 (4)	-0.4039 (3)	-0.6970 (2)	2.1 (2)
C(16)	-1.1618 (4)	-0.3321 (3)	-0.7698 (2)	2.2 (2)
C(17)	-1.0543 (4)	-0.2794 (3)	-0.8094 (2)	2.0 (2)
C(18)	-0.9306 (4)	-0.2998 (3)	-0.7717 (2)	1.6 (1)
C(19)	-0.7373 (4)	-0.3841 (3)	-0.5716 (2)	1.5 (2)
C(20)	-0.6525 (4)	-0.1907 (3)	-0.5646 (2)	2.1 (2)
C(21)	-0.7166 (4)	-0.1688 (3)	-0.6585 (2)	1.7 (2)
C(22)	-0.5970 (4)	-0.4377 (3)	-0.7671 (2)	1.8 (2)
O(22)	-0.5373 (3)	-0.4843 (2)	-0.8266 (2)	2.4 (1)

Table 2. Geometric parameters (Å, °)

C(1)—N(2)	1.502 (5)	C(7)—C(8)	1.539 (6)
C(1)—C(3)	1.556 (5)	C(8)—N(9)	1.471 (5)
C(1)—C(12)	1.556 (5)	N(9)—C(10)	1.473 (5)
C(1)—C(21)	1.536 (5)	N(9)—C(19)	1.458 (5)
N(2)—C(1')	1.364 (5)	C(10)—C(11)	1.547 (5)
N(2)—C(18)	1.440 (5)	C(11)—C(12)	1.572 (5)
C(1')—O(1')	1.216 (5)	C(11)—C(22)	1.518 (5)
C(1')—O(2')	1.344 (5)	C(12)—C(13)	1.492 (5)
O(2')—C(3')	1.457 (5)	C(12)—C(19)	1.530 (5)
C(3)—O(3)	1.402 (5)	C(13)—C(14)	1.367 (5)
C(3)—C(4)	1.581 (5)	C(13)—C(18)	1.394 (5)
C(3)—C(22)	1.521 (5)	C(14)—C(15)	1.391 (6)
C(4)—C(5)	1.550 (5)	C(15)—C(16)	1.386 (5)
C(5)—C(6)	1.538 (5)	C(16)—C(17)	1.393 (6)
C(5)—C(19)	1.537 (5)	C(17)—C(18)	1.401 (6)
C(5)—C(20)	1.527 (5)	C(20)—C(21)	1.559 (5)
C(6)—C(7)	1.531 (6)	C(22)—O(22)	1.207 (5)
N(2)—C(1)—C(3)	118.4 (3)	C(8)—N(9)—C(19)	112.9 (3)
N(2)—C(1)—C(12)	101.1 (3)	C(10)—N(9)—C(19)	108.4 (3)
N(2)—C(1)—C(21)	109.4 (3)	N(9)—C(10)—C(11)	104.0 (3)
C(3)—C(1)—C(12)	100.5 (3)	C(10)—C(11)—C(12)	106.0 (3)
C(3)—C(1)—C(21)	112.6 (3)	C(10)—C(11)—C(22)	113.4 (3)
C(12)—C(1)—C(21)	114.1 (3)	C(12)—C(11)—C(22)	104.1 (3)
C(1)—N(2)—C(1')	122.8 (3)	C(1)—C(12)—C(11)	106.7 (3)
C(1)—N(2)—C(18)	107.2 (3)	C(1)—C(12)—C(13)	103.5 (3)
C(1')—N(2)—C(18)	127.8 (3)	C(1)—C(12)—C(19)	109.8 (3)
N(2)—C(1')—O(1')	125.1 (4)	C(11)—C(12)—C(13)	112.3 (3)
N(2)—C(1')—O(2')	112.2 (3)	C(11)—C(12)—C(19)	103.2 (3)
O(1')—C(1')—O(2')	122.7 (3)	C(13)—C(12)—C(19)	120.7 (3)
C(1')—O(2')—C(3')	114.4 (3)	C(12)—C(13)—C(14)	128.4 (3)
C(1)—C(3)—O(3)	120.0 (3)	C(12)—C(13)—C(18)	109.0 (3)
C(1)—C(3)—C(4)	104.7 (3)	C(14)—C(13)—C(18)	122.5 (3)
C(1)—C(3)—C(22)	102.7 (3)	C(13)—C(14)—C(15)	118.1 (3)
O(3)—C(3)—C(4)	107.3 (3)	C(14)—C(15)—C(16)	120.3 (4)
O(3)—C(3)—C(22)	114.4 (3)	C(15)—C(16)—C(17)	121.8 (4)
C(4)—C(3)—C(22)	106.7 (3)	C(16)—C(17)—C(18)	117.6 (3)
C(3)—C(4)—C(5)	113.7 (3)	N(2)—C(18)—C(13)	109.5 (3)
C(4)—C(5)—C(6)	111.2 (3)	N(2)—C(18)—C(17)	130.9 (3)
C(4)—C(5)—C(19)	112.1 (3)	C(13)—C(18)—C(17)	119.6 (3)
C(4)—C(5)—C(20)	105.0 (3)	C(5)—C(19)—N(9)	117.6 (3)
C(6)—C(5)—C(19)	109.0 (3)	C(5)—C(19)—C(12)	109.2 (3)
C(6)—C(5)—C(20)	111.8 (3)	N(9)—C(19)—C(12)	103.6 (3)
C(19)—C(5)—C(20)	107.6 (3)	C(5)—C(20)—C(21)	109.2 (3)
C(5)—C(6)—C(7)	112.3 (3)	C(1)—C(21)—C(20)	110.8 (3)
C(6)—C(7)—C(8)	109.9 (3)	C(3)—C(22)—C(11)	107.1 (3)
C(7)—C(8)—N(9)	114.1 (3)	C(3)—C(22)—O(22)	126.2 (3)
C(8)—N(9)—C(10)	114.6 (3)	C(11)—C(22)—O(22)	126.7 (3)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55613 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1025]

References

- Camerman, A., Camerman, N. & Trotter, J. (1965). *Acta Cryst.* **19**, 314–320.
 Chiaroni, A., Langlois, N. & Riche, C. (1977). *Acta Cryst.* **B33**, 3410–3414.
 Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* **A24**, 390–397.

- Duchamp, D. J. (1977). *Am. Chem. Soc. Symp. Ser.* No.46, 98–121.
 Duchamp, D. J. (1984). *CRYM. A System of Crystallographic Programs*. The Upjohn Company, Kalamazoo, MI, USA.
 Guggisberg, A., Gorman, A. A., Bycroft, B. W. & Schmid, H. (1969). *Helv. Chim. Acta*, **52**, 76–89.
 Hendrickson, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036–7043.
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 Mills, J. F. D. & Nyburg, S. C. (1960). *J. Chem. Soc.* pp. 1458–1463.
 Ramakrishnan, C. (1980). In *Computing in Crystallography*, edited by R. Diamond, S. Ramaseshan & K. Venkatesan. Bangalore: Indian Academy of Sciences.
 Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 Toffoli, P., Rodier, N., Lewin, G. & Poisson, J. (1986). *Acta Cryst.* **C42**, 1606–1610.

Acta Cryst. (1993). **C49**, 173–175

Structure of 3,3-Dichloro-1*H*-indol-2(3*H*)-one

J. ZUKERMAN-SCHPECTOR

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560 São Carlos, SP, Brazil

ANGELO DA C. PINTO, J. F. M. DA SILVA AND M. T. F. C. BARCELLOS

Instituto de Química, Universidade Federal de Rio de Janeiro, Cidade Universitária, 21910 Rio de Janeiro, RJ, Brazil

(Received 12 May 1992; accepted 29 July 1992)

Abstract

The indol-2-one moiety is essentially planar with a C(2)—C(3) distance of 1.556 (6) Å. Centrosymmetrically related pairs of molecules are linked through hydrogen bonds forming dimers.

Comment

The study of the structural features of isatin (1*H*-indole-2,3-dione) (1) (Palenik, Koziol, Katritzky & Fan, 1990) and its *N*-acetyl derivative, 1-acetylindole-2,3-dione (2) (Zukerman-Schpector, Castellano, Pinto, da Silva & Barcellos, 1992), has led to the observation that in both cases the C(2)—C(3) bond length is significantly longer than the expected value (1.48 Å) for a C(sp²)—C(sp²) single bond; this was ascribed to non-bonded lone pair-