Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods (*MULTAN*80; Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN*.

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Tubingensin B, a Cytotoxic Carbazole Alkaloid from the Sclerotia of *Aspergillus tubingensis*

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Abstract

The crystal structure of tubingensin B, (1α,4α,4aα,7α,-14bβ)-(−)-2,3,4,4a,5,6,7,9-octahydro-4,4a-dimethyl-7-isopropyl-1*H*-7,14b-ethanobenzo[3,4]cyclohepta[1,2-

b]carbazol-1-ol, $C_{28}H_{35}NO$, confirms the structure assigned from NMR spectra. The molecule forms hydrogen-bonded sheets parallel to the *bc* plane in the crystal. A disordered molecule of solvent, $CHCl_3$, is included in the crystal.

Comment

Tubingensin B is a cytotoxic carbazole alkaloid with a novel ring system. It was originally isolated from the sclerotia of the fungus *Aspergillus tubingensis*. Tubingensin B is biogenetically related to other metabolites present in the sclerotia of various *Aspergillus* spp.; some of the metabolites may serve as chemical defenses against consumption of the sclerotia by insects (Gloer, 1995). The structure of the title compound, (I), was assigned on the basis of selective INEPT (insensitive nuclei enhanced by polarization transfer), homonuclear decoupling and COSY (correlation spectroscopy) NMR experiments (TePaske, Gloer, Wicklow & Dowd, 1989). The crystal structure analysis confirms the assigned structure.

(I)
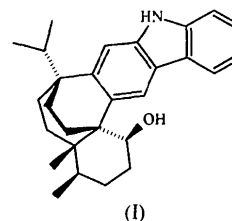
The C4–C9 ring is planar (largest deviation from planarity is 0.018 Å for C6). The C2—C3—C10—C11—C12—C27 ring is distorted slightly from planarity to a C11—C12 half-chair conformation [the C10—C11—C12—C27 torsion angle is 6.9 (5)°]. The N1—C2—C3—C4—C9 ring is also slightly distorted from planarity to the N1 envelope conformation (N1 is 0.044 Å from the C2—C3—C4—C9 plane). The C11—C12—C23—C22—C21—C20 ring has a boat conformation. The C15–C20 ring has a chair conformation. The C13—C14—C15—C20—C21—C22—C23 and the C11—C12—C23—C13—C14—C15—C20 seven-membered rings adopt the chair conformation, with the C13, C15, C20 and C23 atoms forming the seat of the chair for both seven-membered rings.

Four symmetry-related molecules are joined by hydrogen bonds (two unique and two related by twofold symmetry). The molecules alternate as donor and acceptor, forming a ring. Each molecule is also involved in a hydrogen bond of a symmetry-related ring of four molecules, thus forming hydrogen-bonded sheets parallel to the *ab* plane. The geometries of the unique hydrogen bonds are given in Table 2.

As the $CHCl_3$ solvent molecule is near a crystallographic twofold axis, the molecule is necessarily disordered. It is further disordered in that it has two orientations with occupancies of 0.30 (1) for orientation *A*

and 0.22 (1) for orientation *B*. High thermal motion is evident for both orientations.
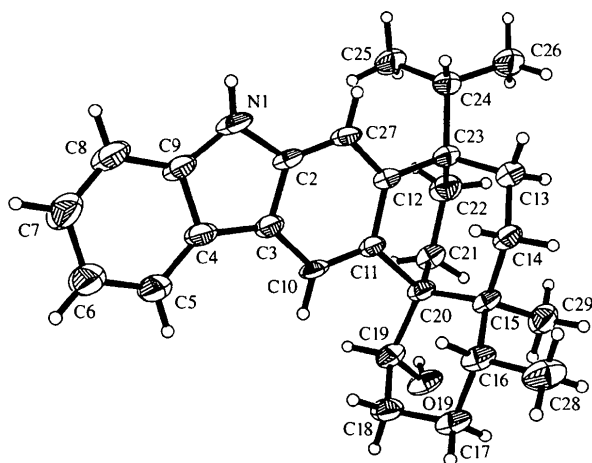

Fig. 1. *ORTEP*II (Johnson, 1976) illustration of the title compound. Displacement ellipsoids are drawn at the 35% probability level.
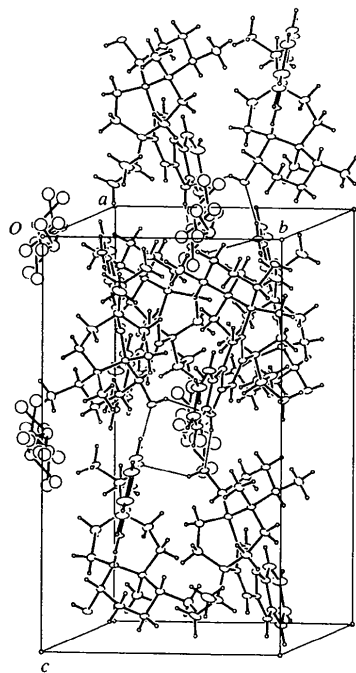

Fig. 2. The contents of the unit cell. The view is approximately perpendicular to the hydrogen-bonded ring. Displacement ellipsoids are represented at the 15% probability level. Hydrogen bonds are shown as thin bonds. The chloroform atoms are represented as spheres of arbitrary radii.

Experimental

Details of the isolation and crystallization of the title compound are given in TePaske *et al.* (1989).

Crystal data

$C_{28}H_{35}NO.0.5CHCl_3$
$M_r = 461.28$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
$C222_1$
$a = 22.212\,(5)$ Å
$b = 11.646\,(4)$ Å
$c = 19.681\,(4)$ Å
$V = 5091\,(2)$ Å^3
$Z = 8$
$D_x = 1.20$ Mg m^{-3}
D_m not measured

Cell parameters from 23
    reflections
$\theta = 9–19°$
$\mu = 0.223$ mm^{-1}
$T = 291$ K
Needle
$0.30 \times 0.15 \times 0.11$ mm
Yellow

Data collection

Enraf–Nonius CAD-4
    diffractometer
$\theta/2\theta$ scans
Absorption correction: none
9411 measured reflections
2369 independent reflections
2108 reflections with
    $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 20°$
$h = -21 \rightarrow 21$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$
3 standard reflections
    frequency: 60 min
    intensity decay: 0.2%

Refinement

Refinement on F^2
$R(F) = 0.0403$
$wR(F^2) = 0.1023$
$S = 1.144$
2369 reflections
332 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 1.3659P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.019$

$\Delta\rho_{max} = 0.158$ e Å^{-3}
$\Delta\rho_{min} = -0.176$ e Å^{-3}
Extinction correction:
    *SHELXL*93 (Sheldrick,
    1993)
Extinction coefficient:
    0.0024 (4)
Scattering factors from
    International Tables for
    Crystallography (Vol. C)
Absolute configuration: not
    determined

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

O19—C19	1.453 (4)	C3—C2	1.394 (5)
N1—C9	1.365 (5)	C3—C4	1.439 (5)
N1—C2	1.407 (4)	C4—C5	1.370 (5)
C11—C10	1.375 (5)	C4—C9	1.417 (5)
C11—C12	1.434 (5)	C9—C8	1.378 (5)
C10—C3	1.411 (5)	C2—C27	1.365 (5)
C9—N1—C2	109.1 (3)	N1—C9—C4	109.1 (3)
C10—C11—C12	119.4 (3)	C8—C9—C4	120.8 (4)
C10—C11—C20	123.2 (3)	C27—C2—C3	122.0 (3)
C12—C11—C20	117.3 (3)	C27—C2—N1	130.0 (3)
C11—C10—C3	120.9 (3)	C3—C2—N1	107.9 (3)
C2—C3—C10	118.2 (3)	C2—C27—C12	120.2 (3)
C2—C3—C4	107.8 (3)	C27—C12—C11	118.9 (3)
C10—C3—C4	134.0 (3)	C27—C12—C23	122.6 (3)
C5—C4—C9	118.7 (3)	C11—C12—C23	118.5 (3)
C5—C4—C3	135.3 (3)	O19—C19—C18	103.3 (3)
C9—C4—C3	106.0 (3)	O19—C19—C20	111.4 (3)
N1—C9—C8	130.1 (3)	C18—C19—C20	117.7 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O19—H19···N1^i	0.82 (5)	2.56 (6)	3.268 (6)	146 (2)
N1—H1···O19^{ii}	0.84 (5)	2.20 (6)	3.024 (6)	169 (2)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The solvent molecule was modeled as a rigid group (C—Cl = 1.77, tetrahedral angles) with two orientations; *A*: C*A*, Cl1*A*, Cl2*A*, Cl3*A*; and *B*: C*B*, Cl1*B*, Cl2*B*, Cl3*B*. The C atoms were given independent isotropic displacement parameters and the displacement

parameters of the Cl atoms were allowed to refine anisotropically. The H atoms were not included in the model. The coordinates of the H atoms involved in the hydrogen bonds (H4 and H19) were allowed to refine. Isotropic displacement parameters equal to $1.2U_{eq}$ of the atom covalently bonded to the H atom were used.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods (*MULTAN*80; Main *et al.*, 1980). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN*.

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Phenylpyruvic Acid

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Abstract

The title compound, $C_9H_8O_3$, determined as the enolic form, 2-hydroxy-3-phenylpropenoic acid, has a fully extended pyruvic side chain. An intramolecular hydro-

gen bond is formed between the enol and the carboxyl O atoms. The molecules are held together by hydrogen bonds between the carboxyl groups. The O···O distances of the intra- and intermolecular hydrogen bonds are 2.639 (3) and 2.673 (3) Å, respectively.

Comment

The title compound is a well known metabolite of phenylalanine, which is a deaminated product of phenylalanine, the deamination catalysed by transaminase. The title compound is present in the urine and blood of a phenylketonuria patient (Martin, Mayes & Rodwell, 1983). To date, however, its crystal structure has not been determined. Accurate information on its structure and conformation is important for understanding its physicochemical role in the metabolic pathway.
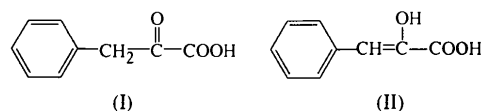
The molecular structure of the title compound is shown in Fig. 1, with the unit-cell packing shown in Fig. 2. The structural formula of the title compound has usually been given in its ketonic form, (I). However, our results show the molecule has the enolic form, (II), a tautomer of the ketonic one. As a result of tautomerism, the π electron in a double bond of the keto group is transferred to C7=C8 [1.339 (3) Å]. The phenyl and carboxyl groups are *trans* to each other about the C7=C8 double bond. The enolic O3 and the carboxyl O2 atoms form an intramolecular hydrogen bond [O3···O2 2.639 (3) Å]. Three torsion angles, O1—C9—C8—O3 −176.2 (3)°, C1—C7—C8—C9 175.5 (3)° and C8—C7—C1—C6 18.6 (4)°, indicate that the structure of this compound is characterized by an almost planar and fully extended conformation.

At present, no structural information is available on the enzymatic recognition mechanism of phenylpyruvic acid for producing further metabolites such as phenyllactic acid or phenylacetic acid. It may be important to consider the planar conformation of the enolic form
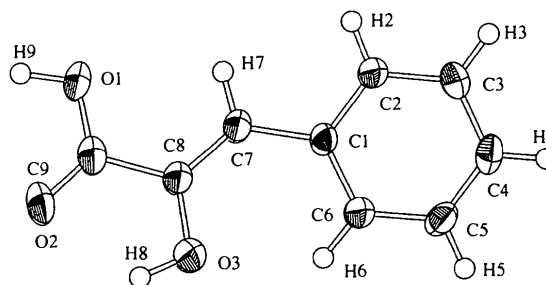
Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.