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Tylophorine B benzene solvate

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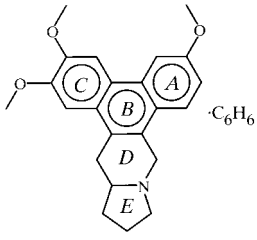
The crystal structure of tylophorine B (or 2,3,6-trimethoxyphenanthro[9,10-*f*]indolizidine) as the benzene solvate, $C_{23}H_{25}NO_3{\cdot}C_6H_6$, has been determined. The compound was isolated from *albizzia julibrissin* and this is the first definitive report of the steochemistry of tylophorine.

Comment

Phenanthroindolizidine (tylophorine) and autofine have been reported to have antitumor and antibiotic effects. We have, for the first time, isolated tylophorine B from *albizzia julibrissin* in a search for interesting bioactive drugs. The title compound, (I), was extracted from the dried bark of silk trees which grow widely in the northwest of China. In traditional Chinese medicine, tylophorine B is used for pain relief, invigorating the circulation of the blood, treating insomnia and asthma, and the removal of strains. The flowers of silk trees are used to make tea to treat sore throat.



(I)

The MS–IR and NMR data suggest that the structure of (I) is consistent with that reported by Li *et al.* (1989). Although the molecular formulae of some similar and closely related compounds have also been reported (Cave *et al.*, 1989; Mitra *et al.*, 1996; Wadhawan & Sikka, 1976), the three-dimensional structure of tylophorine has not been determined until now.

The structure of tylophorine B (Fig. 1) shows a conjunction of phenanthro and indolizidine moieties. The aromatic rings lie almost in the same plane, with dihedral angles of only 1.7 (2) (*A*/*B*), 2.8 (2) (*B*/*C*) and 2.2 (2)° (*A*/*C*). The observed bond lengths and angles are normal in their alternate single- and double-bond display. The *D* ring, consisting of atoms C19, C20, C13 and C14, forms a plane with N1 above [0.338 (10) Å] and C15 below [0.325 (12) Å]. The *B* ring is almost coplanar with ring *D*. The *E* ring adopts an envelope conformation and makes a dihedral angle of 6.7 (3)° with ring *D*. The dihedral angle between the *B* and *D* rings is 7.3 (2)°.

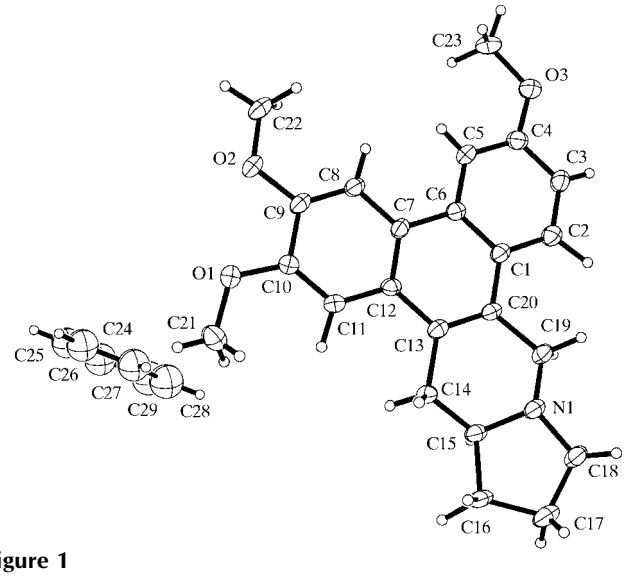


Figure 1
A view of tylophorine B showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

The benzene molecules are held very loosely in the crystal structure with apparently no strong hydrogen-bond interactions.

Experimental

The dry bark of *albizzia julibrissin* (2.3 kg) was powdered and extracted with EtOH (333–343 K) at room temperature. The extract was concentrated and then developed repeatedly by silica-gel chromatography using EtOAc as the developing solvent to yield tylophorine and a number of other known compounds. The dried tylophorine powder is yellow and crystallization in commonly used solvents is difficult. The sample used in this study was recrystallized from a benzene/acetone solution (2:8).

Crystal data

$C_{23}H_{25}NO_3{\cdot}C_6H_6$	$Z = 1$
$M_r = 441.55$	$D_x = 1.273$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 5.393$ (1) Å	Cell parameters from 25 reflections
$b = 9.130$ (2) Å	$\theta = 10$–$20°$
$c = 11.963$ (2) Å	$\mu = 0.082$ mm^{-1}
$\alpha = 92.67$ (3)°	$T = 293$ (2) K
$\beta = 95.02$ (3)°	Block, pale yellow
$\gamma = 100.45$ (3)°	0.5 × 0.4 × 0.3 mm
$V = 575.8$ (2) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$h = 0 \rightarrow 6$
$\theta/2\theta$ scans	$k = -11 \rightarrow 11$
2510 measured reflections	$l = -14 \rightarrow 14$
2510 independent reflections	3 standard reflections
1992 reflections with $I > 2\sigma(I)$	frequency: 60 min
$\theta_{max} = 27.77°$	intensity decay: <0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1522P)^2 + 0.0106P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$(\Delta/\sigma)_{max} = 0.028$
$wR(F^2) = 0.193$	$\Delta\rho_{max} = 0.48$ e Å^{-3}
$S = 1.131$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
2510 reflections	
281 parameters	
H-atom parameters constrained	

The intensities of higher θ angle reflections were very weak due to both the large thermal motion of benzene and the poor crystal quality. This is also reflected in the R value obtained using all the data. The benzene solvent was treated as a fixed planar hexagon with individual isotropic displacement parameters for the C atoms. Attempts to use anisotropic displacement parameters did not result in a chemically realistic model. The absolute configuration was based on related chemistry.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN*/*PC* (Fair, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*/*PC* (Siemens, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1256). Services for accessing these data are described at the back of the journal.

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