Acta Cryst. (1978). B**34**, 3778–3780

Aristotelinine

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(*Received* 3 *February* 1978; *accepted* 16 *June* 1978)

Abstract. $C_{20}H_{26}N_2O_2$, $M_r = 326{\cdot}1994$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}710\,(4)$, $b = 10{\cdot}115\,(1)$, $c = 13{\cdot}035\,(4)$ Å, $U = 1675{\cdot}9\,(8)$ Å^3, $Z = 4$, $D_c = 1{\cdot}294$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $R = 0{\cdot}045$ for all 1532 observed reflections. Aristotelinine, (3*S*,4a*S*,5*R*,10b*R*,11a*R*,13*R*)-1,2,3,4,4a,5,11,11a-octahydro-2,2,5-trimethyl-3,5-ethano-10b*H*-pyrido[3,2-*b*]carbazole-10b,13-diol, is a unique indole-type alkaloid isolated from the leaves and stems of *Aristotelia chilensis*. The nature of the ring fusions and the tertiary hydroxyl group in the five-membered ring of the indole moiety are interesting features of this alkaloid.

Introduction. *Aristotelia chilensis* (Mol.) Stuntz (Eleocarpaceae) has yielded a series of alkaloids which are unique to the genus *Aristotelia* (Bittner, Silva, Gopalakrishna, Watson, Zabel, Matlin & Sammes, 1978). An analysis of the various structures has led to the postulation of a new biosynthetic pathway and the title compound is an intermediate in the biosynthesis of the more highly strained members of the series.

Aristotelinine forms long colorless needles and a sample of dimensions 0·1 × 0·1 × 0·2 mm was cleaved from a larger crystal. The unit cell was found to be orthorhombic and room-temperature cell dimensions were obtained by a least-squares fit to 15 medium-angle reflections. Systematic absences, $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$ and $00l$ when $l \neq 2n$, are consistent with space group $P2_12_12_1$. Intensity data with $2\theta < 140°$ were collected on a Syntex $P2_1$ diffractometer by the $\theta{:}2\theta$ scan technique using graphite-monochromated radiation and a variable scan speed. A periodically-monitored check reflection showed no significant crystal deterioration. Of the 1532 independent reflections measured, 1309 had intensities greater than $3\sigma(I)$ where $\sigma(I)$ was estimated from counting statistics. Negative measured intensities were assigned the value of zero. Lorentz and polarization corrections were applied but no absorption corrections were made.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) to calculate phases for the 450 $|E_{\mathbf{h}}|$ values greater than 1·03. Fifty reflections with $E_{\mathbf{h}} = 0$ were included for the Ψ_0 test. The E map computed from the phase set with the highest combined figure of merit revealed clearly all 24 non-hydrogen atoms. A structure factor calculation with all atoms designated as C atoms gave an R factor of 0·24 where $R = [\sum \Delta F_{\text{meas}}/\sum |F_{\text{meas}}|]$. Least-squares refinement with isotropic thermal parameters and appropriate scattering factors reduced R to 0·13. Least-squares refinement with anisotropic thermal parameters reduced R to 0·075, and a difference map computed with these phases revealed the positions of all H atoms. Least-squares refinement with isotropic H atom thermal parameters yielded a final R value of 0·045 for all 1532 reflections. The function minimized

Table 1. *Atomic positional parameters* (× 10^4) *for aristotelinine*

	x	y	z
N(1)	7465 (2)	3746 (3)	7807 (2)
C(2)	8389 (3)	3589 (4)	7112 (3)
C(3)	8024 (3)	3644 (4)	5985 (3)
C(4)	7378 (3)	4885 (4)	5785 (3)
C(4a)	6403 (3)	4845 (3)	6471 (3)
C(5)	5686 (3)	3661 (4)	6171 (2)
C(5a)	4866 (3)	3537 (3)	7001 (2)
N(6)	3862 (2)	3518 (3)	6840 (2)
C(6a)	3364 (3)	3560 (3)	7826 (2)
C(7)	2282 (3)	3557 (4)	8004 (3)
C(8)	1962 (4)	3630 (4)	9023 (4)
C(9)	2671 (4)	3708 (5)	9810 (3)
C(10)	3750 (3)	3699 (4)	9624 (3)
C(10a)	4080 (3)	3620 (4)	8615 (2)
C(10b)	5164 (3)	3593 (4)	8146 (2)
C(11)	5825 (3)	4830 (4)	8318 (3)
C(11a)	6756 (3)	4877 (3)	7591 (3)
C(12)	6310 (3)	2347 (4)	6084 (3)
C(13)	7401 (3)	2448 (4)	5600 (3)
C(14)	8889 (4)	2270 (5)	7381 (4)
C(15)	9205 (4)	4709 (7)	7290 (5)
C(16)	5139 (4)	3956 (7)	5152 (3)
O(17)	5693 (2)	2430 (3)	8488 (2)
O(18)	7274 (2)	2564 (4)	4507 (2)

Table 2. *Internal torsion angles for aristotelinine* (°)

Ring *A*		Ring *B*		Ring *C*		Ring *D*	
6a–7	0·6	5a–6	0·1	4a–5	45·6	1–2	−49·9
7–8	0·3	6–6a	0·6	5–5a	−46·0	2–3	53·0
8–9	−0·9	6a–10a	−1·1	5a–10b	51·5	3–4	−61·3
9–10	0·6	10a–10b	1·0	10b–11	−53·7	4–4a	63·2
10–10a	0·3	10b–5a	−0·7	11–11a	58·4	4a–11a	−58·0
10a–6a	−0·9			11a–4a	−55·0	11a–1	53·1

Ring *E*		Eight-membered ring	
3–4	67·3	1–2–3–13	−71·1
4–4a	−64·3	2–3–13–12	69·3
4a–5	49·3	3–13–12–5	43·1
5–12	−39·2	13–12–5–4a	−39·2
12–13	43·1	12–5–4a–11a	−74·5
13–3	−56·2	5–4a–11a–1	66·6
		4a–11a–1–2	53·1
		11a–1–2–3	−49·9

was $\sum w(\Delta F_{\text{meas}})^2$ where $w = 1/\sigma^2(F)$. The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974).

All parameter shifts during the final cycle were less than $0{\cdot}3\sigma$, and a final difference map showed no peak larger than 0·14 e Å^{-3}. The positional parameters are given in Table 1.*

Discussion. Fig. 1 shows an *ORTEP* drawing (Johnson, 1965) of the solid-state conformation. The absolute configuration of aristotelinine has been inferred from that of aristoteline (Anderson *et al.*, 1975). Bond lengths and angles are indicated in Figs. 2 and 3.

Least-squares planes fitted to the phenyl and five-membered rings show maximum deviations from planarity of 1σ while a least-squares plane fitted to both rings shows deviations of less than 2σ. The indole system is planar.

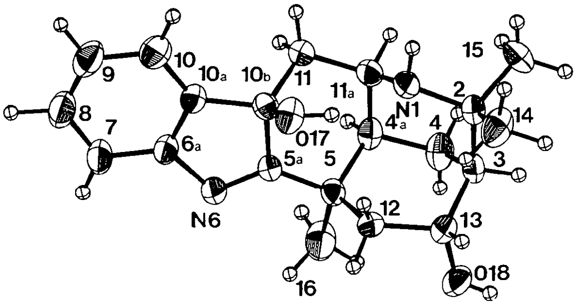

Fig. 1. *ORTEP* drawing of aristotelinine. Anisotropic thermal parameters are drawn at 50% probability level while hydrogen atoms are represented by spheres of arbitrary size.

Torsion angles for the various ring systems in aristotelinine are listed in Table 2. The internal torsion angles for the cyclohexane *C* ring indicate considerable deviation from the expected value of 56° (Bucourt, 1974). The ring is *cis*-fused to the heterocyclic *D* ring and *cis*-fused to the six-membered *E* ring. A flattening of the torsion angles associated with C(5a), C(5) and C(4a) is due primarily to planarity imposed by the N(6)—C(5a) double bond. An intramolecular hydrogen bond is formed between the 1,3-diaxial substituents

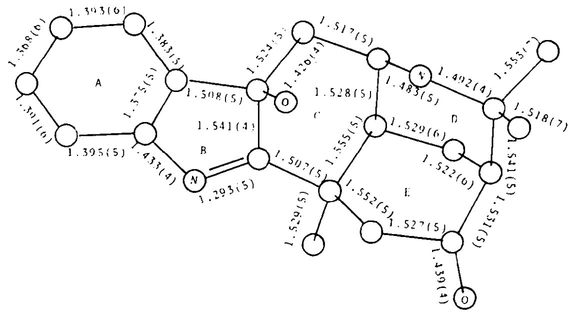

Fig. 2. Bond lengths (Å) for aristotelinine. Ring-system labels and nitrogen and oxygen atoms are indicated in the figure.

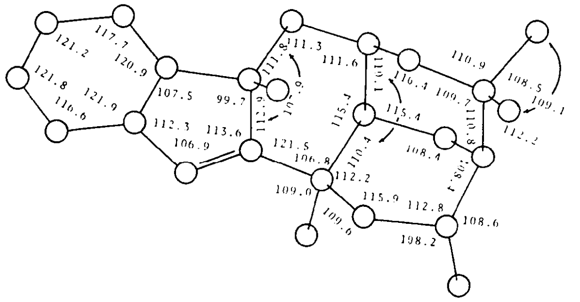

Fig. 3. Valence angles (°) for aristotelinine. Standard deviations are 0·3 and 0·4°.

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* Lists of structure factors, anisotropic and isotropic thermal parameters, and positional parameters (for H atoms) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33706 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(17) and N(1). This interaction does not result in any severe changes in torsion angles.

The heterocyclic *D* ring is *cis*-fused to ring *C* and 1,3-diaxially fused to ring *E*. Alternatively, it can be considered to be a component of a bridged eight-membered ring. There are several opposing interactions which determine the torsion angles in the heterocyclic six-membered ring. The fusion of the C(4a) and C(3) axial substituents tends to increase the torsion angles while interactions $H(4\alpha)\cdots H(15\gamma) = 2{\cdot}04$, $H(11a)\cdots H(15\gamma) = 2{\cdot}33$ and $H(12\beta)\cdots N(1) = 2{\cdot}72$ Å tend to flatten the ring and reduce the torsion angles.

Ring *E* is *cis*-fused to ring *C* and 1,3-diaxially fused to ring *D*. The diaxial fusion and interactions $H(12\alpha)\cdots H(16\gamma) = 2{\cdot}51$, $H(12\beta)\cdots N(1) = 2{\cdot}72$ and $H(13)\cdots H(14\beta) = 2{\cdot}23$ Å determine the variations in torsion angles. The eight-membered ring assumes a boat conformation. The H on O(17) is bonded intramolecularly to N(1) with $N(1)\cdots O(17) = 2{\cdot}763$, $N(1)\cdots H(17) = 2{\cdot}11$ and $H(17)\cdots O(17) = 0{\cdot}87$ Å. O(18) is intermolecularly hydrogen bonded to N(6) with $N(6)\cdots O(18) = 2{\cdot}891$, $N(6)\cdots H(18) = 2{\cdot}18$ and $H(18)\cdots O(18) = 0{\cdot}87$ Å.

Aristotelinine can be considered a biological oxidation product of aristoteline. These alkaloids represent a unique structural type which may be restricted to the genus *Aristotelia*.

We would like to acknowledge support for this project by the National Science Foundation (OIP74-21108), the OAS (PMC-8-1) and CONICYT of Chile and the supply of equipment by the National Science Foundation (CHE74-19742). We thank Julio Varga for his technical assistance. FASTBIOS contribution No. 39.

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Acta Cryst. (1978). B**34**, 3780–3781

2,3-Dihydro-2-(4-methoxyphenyl)-3-phenyl-4*H*-1,3,2-benzoxazaphosphorine-4-thione 2-Oxide

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(*Received* 4 *July* 1978; *accepted* 24 *July* 1978)

Abstract. $C_{20}H_{16}NO_3PS$, $M_r = 381{\cdot}4$, monoclinic, $P2_1/c$, $a = 12{\cdot}96\,(2)$, $b = 15{\cdot}60\,(2)$, $c = 9{\cdot}49\,(1)$ Å, $\beta = 103{\cdot}8\,(2)°$, $V = 1863{\cdot}3$ Å^3, $Z = 4$, $D_c = 1{\cdot}36$ g cm^{-3}. Refinement gave $R = 0{\cdot}056$ and $R_w = 0{\cdot}060$ for 235 parameters and 1761 significant reflexions [$I > 3\sigma(I)$]. The stereochemistry of the molecule has been established.

Introduction. The title compound was prepared by Scheibye, Pedersen & Lawesson (1978*a*,*b*) as yellow crystals (m.p. 173 °C). The crystals were kindly provided by S. Scheibye.

A crystal $1{\cdot}0 \times 0{\cdot}7 \times 0{\cdot}2$ mm was mounted about **c**. The lattice type and space group were established from photographs taken with Cu and Mo radiations.

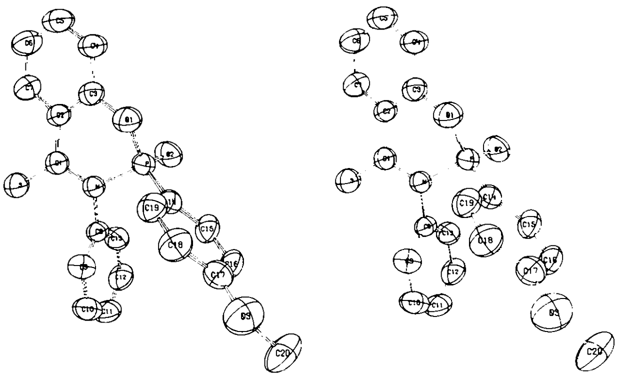

Fig. 1. A stereoscopic drawing of the molecule showing the numbering of the atoms.