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2-Phenylsparteine

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Abstract. $C_{21}H_{30}N_2$, $M_r = 310{\cdot}48$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}586\,(5)$, $b = 14{\cdot}415\,(2)$, $c = 16{\cdot}936\,(4)$ Å, $V = 1851{\cdot}9\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}12$ g cm^{-3}, m.p. = 352–353 K, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·6 cm^{-1}, $F(000) = 680$, $T = 292$ K, final $R = 0{\cdot}044$ for 1489 observed reflections. The quinolizidine moieties both have *trans* configurations, and piperidine rings *A, B, C* and *D* have chair, chair, boat and chair conformations, respectively. The phenyl subtituent at C(2) is equatorial.

Introduction. This structure determination of 2-phenylsparteine (I) continues our studies on sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1978; Szymczak, 1983). Our previous X-ray determinations of 2-phenyl derivatives of sparteine included 2-phenylsparteine *N*(16)-oxide monoperchlorate (Małuszyńska & Okaya, 1977), 2-(*p*-tolyl)-2-dehydrosparteine (Małuszyńska, Boczoń & Kałuski, 1986) and $\Delta^{1(2)}$-dehydro-2-phenylsparteine diperchlorate (Boczoń, Kałuski & Małuszyńska, 1987). The synthesis of 2-phenylsparteine has been described and the configuration of C(2), as well as the configuration of the flexible *C*/*D* moiety, have been determined on the basis of a comparison of IR spectra of this compound with those of monodeuterated derivatives (Boczoń, 1981). The sparteine molecule consists of two quinolizidine moieties (rings *A*–*B* and *C*–*D*). The configuration of the quinolizidine moieties is *trans*–*trans* for α-isosparteine, *trans*–*cis* for sparteine and *cis*–*cis* for β-isosparteine (for molecules with all four piperidine rings in chair conformation). The *trans* form is rigid, while the *cis* form is flexible. Thus, in sparteine and β-isosparteine the inversion of N(16), the conversion of ring *C* from chair to boat, and the change of configuration of moiety *C*/*D* from *cis* to *trans* are possible. These compounds, as free bases in the liquid state and in solution, exist predominantly with ring *C* in the boat form (Bohlmann, Schumann & Arndt, 1965; Skolik, Krueger & Wiewiórowski, 1970). The main aim of this X-ray determination was to confirm the spectroscopic results concerning the conformation of ring *C* and to determine the orientation of the phenyl substituent at C(2).

Experimental. Crystals of (I) suitable for X-ray analysis were obtained from ethanol solution. Colourless elongated plates, crystal dimensions 0·3 × 0·3 × 0·2 mm. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, unit-cell parameters from least-squares fit to 25 reflections ($9{\cdot}9 \leq 2\theta \leq 13{\cdot}7°$), 2θ–θ scan method, variable scan speed (2·0–20·0° min^{-1}) depending on reflection intensity. 1895 reflections up to $2\theta = 50°$ were measured: h 0→9, k 0→17, l 0→6; no systematic variation in intensity was observed for three control reflections measured every 2 h, Lp corrections, no absorption corrections, 1489 reflections with $I \geq 1{\cdot}96\sigma(I)$ were considered observed. The structure was solved by direct methods with *SHELX*76 (Sheldrick, 1976) and the absolute configuration of the molecule was assigned according to the previous determination of the absolute configuration of the naturally occurring sparteine derivatives as C(7) *S* and C(9) *S* (Klyne, Scopes, Thomas, Skolik, Gawroński & Wiewiórowski, 1974). The positions of all H atoms were recalculated from the geometry of the molecule after each cycle of refinement, all H atoms were assigned an equal isotropic temperature factor of

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
N(1)	0·1799 (3)	0·5343 (2)	0·1698 (1)	0·044
C(2)	0·1639 (4)	0·4346 (2)	0·1482 (2)	0·047
C(3)	−0·0169 (4)	0·4138 (2)	0·1126 (2)	0·058
C(4)	−0·1674 (4)	0·4424 (2)	0·1676 (2)	0·066
C(5)	−0·1448 (4)	0·5452 (2)	0·1870 (2)	0·067
C(6)	0·0364 (4)	0·5635 (2)	0·2230 (2)	0·055
C(7)	0·0610 (4)	0·6668 (2)	0·2436 (2)	0·059
C(8)	0·2332 (4)	0·6793 (2)	0·2885 (2)	0·060
C(9)	0·3786 (4)	0·6518 (2)	0·2317 (2)	0·049
C(10)	0·3520 (4)	0·5506 (2)	0·2071 (2)	0·051
C(11)	0·3813 (4)	0·7194 (2)	0·1606 (2)	0·054
C(12)	0·5462 (5)	0·7802 (2)	0·1627 (2)	0·075
C(13)	0·5483 (6)	0·8497 (3)	0·0944 (3)	0·097
C(14)	0·3810 (7)	0·9058 (3)	0·0940 (3)	0·101
C(15)	0·2218 (6)	0·8425 (3)	0·0943 (3)	0·095
N(16)	0·2278 (4)	0·7808 (2)	0·1624 (2)	0·060
C(17)	0·0617 (4)	0·7293 (2)	0·1696 (2)	0·067
C(18)	0·3059 (4)	0·4065 (2)	0·0902 (2)	0·048
C(19)	0·3920 (5)	0·3218 (2)	0·0980 (2)	0·060
C(20)	0·5165 (5)	0·2938 (3)	0·0427 (2)	0·076
C(21)	0·5566 (5)	0·3496 (3)	−0·0200 (3)	0·084
C(22)	0·4725 (6)	0·4337 (3)	−0·0288 (2)	0·079
C(23)	0·3479 (5)	0·4619 (2)	0·0256 (2)	0·065

0·07 Å^2. The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = \sigma^{-2}(F_o)$, final $R = 0·044$, $wR = 0·039$, $S = 1·7$, $(\Delta/\sigma)_{max} = 0·002$, the highest and the lowest peaks on the final ΔF map were 0·11 and $-0·14$ e Å^{-3}. Most of the calculations were performed with *SHELX*76 (Sheldrick, 1976), atomic scattering parameters as incorporated in this program, IBM XT-Turbo computer. The final atomic parameters are listed in Table 1.*

Discussion. The bond lengths and valency angles are given in Fig. 1. They are similar to those observed in other sparteine derivatives; charactertistic features are sharpening of angle C(7)—C(8)—C(9) and widening of C(6)—C(7)—C(17) and C(10)—C(9)—C(11) or N(1)—C(10)—C(9) and C(7)—C(17)—N(16) in the region of fusion of the two quinollizidine moieties. There are no significant differences in bond lengths and valency angles between the two quinolizidine moieties, except for bonds about C(2) and C(15). The C(2)—C(18) bond length agrees with the length of a single C_{sp^3}—C_{sp^2} bond (1·510 Å; Allmann, 1977). In the phenyl ring the largest departure from the ideal angle of 120° is observed for C(19)—C(18)—C(23), as was also observed for 2-(*p*-tolyl)-2-dehydrosparteine (Małuszyńska, Boczoń & Kałuski, 1986). No significant distortion from planarity is observed for the phenyl ring.

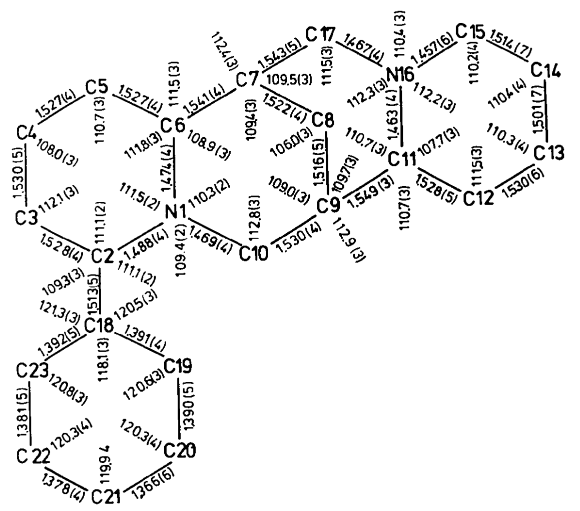

Fig. 1. Bond lengths (Å) and valency angles (°).

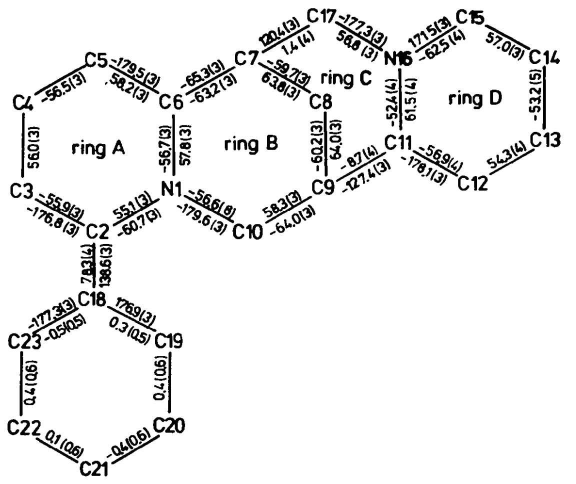

Fig. 2. Torsion angles (°). The endocyclic torsion angles are given inside the rings while the exocyclic angles are given outside the molecular contour and are defined by the bonds along the outline of the molecule.

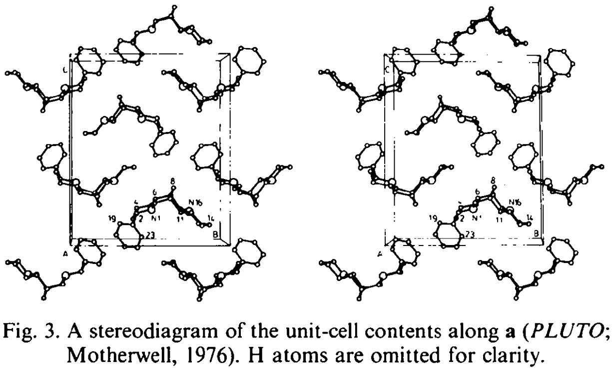

Fig. 3. A stereodiagram of the unit-cell contents along **a** (*PLUTO*; Motherwell, 1976). H atoms are omitted for clarity.

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51996 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The torsion angles are given in Fig. 2. The piperidine rings *A, B, C* and *D* have chair, chair, boat and chair conformations, respectively. The position of the phenyl ring can be conveniently described by the torsion angles along C(2)—C(18) (see Fig. 2). The corresponding torsion angles in 2-phenylsparteine *N*(16)-oxide perchlorate (Małuszyńska & Okaya, 1977) have very similar valules of 137·0 (6) and 76·8 (8)°; a similar orientation of the phenyl ring was also observed in 2-(*p*-tolyl)-2-dehydrosparteine [torsion angles 132·9 (7) and −44·6 (9)°].

A stereoview of the unit-cell contents of (I) is presented in Fig. 3. No intermolecular contacts shorter than van der Waals distances were observed.

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Non-Natural 14-Hydroxy Steroids. I. Methyl 14β-Hydroxy-1,7,17-trioxo-5β,8α,9β-androstan-10β-oate

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Abstract. $C_{20}H_{26}O_6$, $M_r = 362{\cdot}42$, monoclinic, $A2/n$, $a = 16{\cdot}6256\,(8)$, $b = 10{\cdot}6293\,(5)$, $c = 20{\cdot}3059\,(6)$ Å, $\beta = 91{\cdot}515\,(3)°$, $V = 3587{\cdot}17\,(7)$ Å^3, $D_x = 1{\cdot}342$ Mg m^{-3}, $Z = 8$, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}54056$ Å, $\mu = 0{\cdot}77$ mm^{-1}, $F(000) = 1552$, room temperature, final $R = 0{\cdot}039$ for 3207 observed reflections. The non-natural steroid compound bears a methoxycarbonyl group at C(10). The relative stereochemistry is *cis* for the *A*/*B* ring junction, *syn* between MeO_2C—C(10) and H—C(9), *trans* for the *B*/*C* ring junction, *anti* between H—C(8) and HO—C(14) and *cis* for the *C*/*D* ring junction, and an all-chair conformation is adopted.

Introduction As part of a study aimed at the synthesis of various natural and non-natural 14-hydroxy steroids, compound (1) was obtained upon acidic or alkaline treatment of the tetraketone (2) (Ruel & Deslongchamps, 1988). One could predict the stereochemical identity of the C(14) carbon center as that shown in structure (1), based on related work (Yates, Douglas, Datta & Sawyer, 1988) which reported the synthesis of the 14β-hydroxy steriod (3) by a similar approach. Unequivocal assignment of the structural identity of the steroidal compound (3) was made by X-ray analysis (Douglas, Sawyer & Yates, 1987). The present crystallographic analysis was undertaken to confirm the predicted structure of steriod (1) (Fig. 1).

Experimental. Crystal 0·20 × 0·15 × 0·30 mm; Enraf–Nonius CAD-4 diffractometer graphite-monochromator, Cu $K\bar{\alpha}$ radiation; cell dimensions were obtained from 28 reflections with 2θ angles in the range 80·0–120·0°. The $\omega/2\theta$ scan mode was used for data collection at a constant scan speed of 4° min^{-1}.

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