pronounced overlap between a C=O bond and a phenyl ring of adjacent moelcules; this C=O···phenyl interaction has been observed by Ueno, Nakanishi, Hasegawa & Sasada (1978, and references therein) in a family of symmetrically substituted diolefins.

This molecular stacking along the 7 Å axis brings parallel non-equivalent C=C bonds at a distance of 4·04 Å, which is a prerequisite for the feasibility of a $(2\pi + 2\pi)$ photocycloaddition reaction in the crystalline state (Schmidt, 1971). In fact, photodimers and photopolymers of (II) were obtained, isolated, characterized, and their absolute configuration deduced from that of the monomer crystal (Addadi & Lahav, 1978).

The thermal parameters of the atoms were found to be very high, especially those of the atoms which lie on the periphery of the molecule, and the methyl atoms of the ethyl and *sec*-butyl groups. This seems to indicate a high vibrational motion due to weak crystal forces; the high thermal parameters of the *sec*-butyl group, however, could also result from the fact that the data were measured on a non-optically-pure crystal, containing 5% of the enantiomer in the form of a solid solution (Addadi &Lahav, 1979*b*). This was not taken care of explicitly in the refinement.

I thank Dr Nakanishi for providing details of the crystal structure of di-*n*-propyl *p*-phenylene-di-α-cyano-(*E*)-acrylate prior to publication, E. Gati for growing the crystals and L. Addadi, M. Lahav and L. Leiserowitz for useful discussions.

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17-Oxosparteine

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Abstract. $C_{15}H_{24}N_2O$, orthorhombic, $P2_12_12_1$, a = 6·945 (1), b = 9·085 (1), c = 21·857 (3) Å, Z = 4, D_c = 1·20 Mg m^{-3}. The final R for 996 reflections is 0·049; R_w = 0·057. The quinolizidine skeletons (systems A/B and C/D) have the *trans–trans* configuration. The piperidine rings A, B, C and D have chair, chair, sofa and chair conformations respectively.

Introduction. 17-Oxosparteine is the first of the group of 'oxo' sparteine derivatives we have investigated. These compounds have already been examined by spectroscopic methods (Wiewiórowski & Lompa-Krzymień, 1969, 1970). From our measurements we explain the influence of the 'oxo' substituent on the conformation and molecular structure of the sparteine skeleton; *e.g.* on the N(1)–N(16) distance, the inclination of one quinolizidine skeleton to the other, and the C–N bond distance in the lactam group.

Colorless crystals of 17-oxosparteine were obtained from methanol solution. The dimensions of the crystal used for data collection were 0·4 × 0·4 × 0·3 mm. The measurements were performed on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu $K\alpha$ radiation. The θ–2θ scan method was used with a variable scan speed (minimum: 2° min^{-1}; maximum: 29·3° min^{-1}), depending on the reflection intensity. A control reflection was monitored after every 57 reflections. 1090 reflections were collected, including systematic absences; 996 had intensities greater than $1{\cdot}96\sigma_I$, and were included in the refinement. Only the Lorentz and polarization corrections were applied.

The structure was solved by direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). All nonhydrogen atoms were found on the E map based on the correct phase set. The refinement of the positions and anisotropic temperature factors of the nonhydrogen atoms was followed by the difference Fourier map, from which all H atoms were located.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters*

	x	y	z	B_i (Å^2)
N(1)	2358 (5)	2304 (4)	6855 (1)	4·1 (2)
N(16)	2616 (4)	452 (4)	5967 (1)	4·4 (2)
C(2)	1717 (6)	3179 (5)	7377 (2)	5·0 (3)
C(3)	−394 (7)	3612 (6)	7323 (2)	6·7 (4)
C(4)	−735 (7)	4453 (5)	6722 (2)	6·1 (3)
C(5)	8 (7)	3506 (5)	6916 (2)	5·2 (3)
C(6)	2100 (6)	3101 (5)	6277 (2)	4·3 (3)
C(7)	2902 (6)	2186 (5)	5749 (2)	4·3 (2)
C(8)	5050 (6)	1961 (5)	5832 (2)	5·0 (3)
C(9)	5267 (5)	1064 (5)	6420 (2)	4·3 (2)
C(10)	4389 (6)	1921 (5)	6949 (2)	4·6 (3)
C(11)	4412 (5)	−458 (5)	6331 (2)	4·2 (2)
C(12)	5831 (7)	−1535 (6)	6031 (2)	5·7 (3)
C(13)	4488 (8)	−3039 (5)	5927 (2)	6·5 (3)
C(14)	3096 (8)	−2940 (5)	5582 (2)	5·8 (3)
C(15)	1745 (7)	−1909 (5)	5895 (2)	5·6 (3)
C(17)	1845 (6)	2730 (5)	5684 (2)	4·4 (3)
O	649 (5)	635 (4)	5838 (1)	6·4 (2)
H(2)	258	424	738	7·0
H(2′)	183	257	776	7·0
H(3)	385	247	273	7·0
H(3′)	445	80	233	7·0
H(4)	−11	39	825	7·0
H(4′)	259	16	334	7·0
H(5)	419	246	389	7·0
H(5′)	−17	397	585	7·0
H(6)	292	416	634	7·0
H(7)	280	289	537	7·0
H(8)	79	211	420	7·0
H(8′)	45	342	453	7·0
H(9)	171	420	350	7·0
H(10)	447	125	735	7·0
H(10′)	13	204	298	7·0
H(11)	93	90	177	7·0
H(12)	386	376	934	7·0
H(12′)	299	332	874	7·0
H(13)	412	120	932	7·0
H(13′)	19	365	121	7·0
H(14)	180	261	14	7·0
H(14′)	245	397	53	7·0
H(15)	377	228	124	7·0
H(15′)	451	171	67	7·0

The H atoms were assigned isotropic temperature factors and were not included in the refinement. The final R value for 996 reflections was 0·049.* The function minimized was $\sum w(F_o - F_c)^2$, where $w = \sigma_{F_o}^{-2}$. In the last three cycles of refinement the following weighting scheme was used: $w = (F_o/1\cdot65)^2$ for $F_o < 1\cdot65$; $w = 1$ for $1\cdot65 \le F_o \le 11\cdot34$; $w = (11\cdot34/F_o)^2$ for $11\cdot34 < F_o$. The final positional parameters are listed in Table 1. All programs were from the Syntex *XTL/E-XTL* structure determination system (Syntex, 1976).

Discussion. Fig. 1 shows the bond lengths and angles of 17-oxosparteine. All are in good agreement with those obtained for similar sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1978). Torsion angles in Fig. 2 show that rings *A*, *B*, *C* and *D* have chair, chair, sofa and chair conformations respectively. Fig. 3 is an *ORTEP* drawing (Johnson, 1965) of the molecule at 50% probability. The asymmetry parameters (Duax & Norton, 1975) are:

ring *A*

$$\Delta C_2^{4,3} = 0\cdot1, \quad \Delta C_s^{2,5} = 2\cdot6, \quad \Delta C_s^{3} = 1\cdot5°;$$

ring *B*

$$\Delta C_s^{7} = 2\cdot8, \quad \Delta C_2^{1,6} = 7\cdot0, \quad \Delta C_s^{1} = 3\cdot7°;$$

ring *C*

$$\Delta C_s^{8,16} = 7\cdot8, \quad \Delta C_s^{9,17} = 59\cdot9, \quad \Delta C_2^{8,9} = 21\cdot2°;$$

ring *D*

$$\Delta C_2^{2,13} = 0\cdot5, \quad \Delta C_s^{11,16} = 5\cdot1, \quad \Delta C_s^{12,15} = 2\cdot6°.$$

The previous spectroscopic measurements (Wiewiórowski & Lompa-Krzymień, 1970) suggested the all-chair conformation for the free base in $CDCl_3$ solution.

The distance N(1)—N(16) is 3·173 (4) Å; that is, significantly longer than that obtained for α-isosparteine (Przybylska & Barnes, 1953), even if we take into account the low accuracy of their data.

Characteristic angles for the inclination of one quinolizidine skeleton with respect to the other are: C(6)—C(7)—C(17) = 111·1 (3), C(10)—C(9)—C(11) = 114·0 (3), C(7)—C(8)—C(9) = 106·1 (3)°. The C(17)—

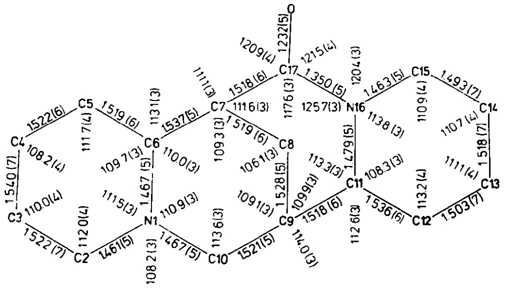

Fig. 1. Bond lengths (Å) and angles (°) for 17-oxosparteine.

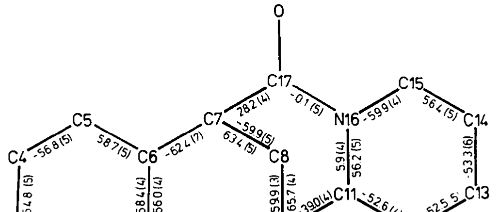

Fig. 2. Torsion angles (°) for 17-oxosparteine.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35287 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

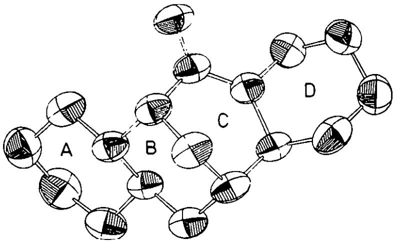

Fig. 3. *ORTEP* drawing of 17-oxosparteine.

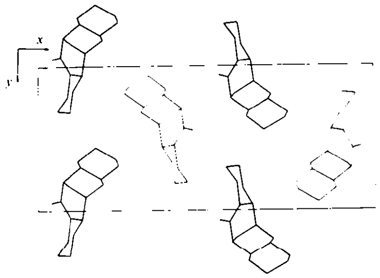

Fig. 4. Unit-cell contents and molecular packing of 17-oxosparteine.

N(16) bond distance in the lactam group is 1·350 (5) Å, and C(17)—O is 1·232 (5) Å; this indicates a slightly conjugated bond system. Similar values were obtained for the lactam group of (±)-lupanine (Doucerain, Chiaroni & Riche, 1976). The oxo substituent in the 17 position causes a greater flattening of ring *C* in the region of the lactam group than does the oxo substituent in the outer ring [in position C(2)] of (±)-lupanine (Doucerain, Chiaroni & Riche, 1976). The thermal motions of the molecule (Fig. 3) are slightly higher in comparison with those of the other sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1978); this may be connected with the rather low (351 K) melting point of the compound.

The molecular packing of 17-oxosparteine is shown in Fig. 4. There are no intermolecular contacts other than van der Waals interactions.

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Structure of *N*,*N*′-Diacetyl-3-methylthiobenzidine

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Abstract. $C_{17}H_{18}N_2O_2S$, triclinic, $P\bar{1}$, $a = 9{\cdot}702\ (4)$, $b = 11{\cdot}027\ (7)$, $c = 7{\cdot}710\ (2)$ Å, $\alpha = 72{\cdot}09\ (4)$, $\beta = 100{\cdot}19\ (3)$, $\gamma = 97{\cdot}18\ (5)°$, $V = 770{\cdot}3$ Å^3 [at 138 (2) K] and $a = 9{\cdot}709\ (1)$, $b = 10{\cdot}929\ (2)$, $c = 7{\cdot}9983\ (8)$ Å, $\alpha = 73{\cdot}61\ (2)$, $\beta = 101{\cdot}20\ (1)$, $\gamma = 98{\cdot}04\ (2)°$, $V = 795{\cdot}4$ Å^3, $D_o = 1{\cdot}316$, $D_c = 1{\cdot}313$ Mg m^{-3} (at 298 K), $M_r = 314{\cdot}41$, $Z = 2$. The final R value is 0·045 for 2560 reflections. The dihedral angle between the two phenyl rings is 33·7°.

Introduction. *N*,*N*′-Diacetyl-*N*-hydroxybenzidine has been shown to be an *in vitro* metabolite of benzidine in several rodent species and may represent the proximate form of the carcinogen. The compound can be converted in hepatic cytosol to an ultimate carcinogenic electrophile, presumably *N*,*N*′-diacetyl-*N*-sulfonyloxybenzidine. The title compound is obtained when methionine is included in the sulfotransferase incubation (Morton, Beland, Evans, Hulse & Kadlubar, 1980).

Single crystals of the title compound (Fig. 1) were obtained by crystallization from ethyl acetate. A suitable crystal of size 0·43 × 0·30 × 0·19 mm was chosen for data collection. A preliminary examination

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