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6-Acetoxy-5-methoxy-1-methyl-1,2,3,9a-tetrahydrocyclohexa[*ij*]isoquinoline-7-spiro-4′-(2′-methoxy-2′,5′-cyclohexadien-1′-one) Methiodide (Acetyl Dienone II Methiodide)

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(*Received* 10 *June* 1978; *accepted* 25 *August* 1978)

Abstract. $C_{22}H_{25}NO_5.CH_3I$, $M_r = 525{\cdot}4$, m.p. 255 ~ 256 °C (crystallized from methanol solutions), $C2/c$, $a = 20{\cdot}435$ (10), $b = 11{\cdot}899$ (5), $c = 21{\cdot}379$ (10) Å, $\beta = 113{\cdot}74$ (1)°, $U = 4758$ Å^3, $Z = 8$, $D_x = 1{\cdot}467$ g cm^{-3}, μ(Mo $K\alpha$) = 13·6 cm^{-1}. The configuration around the spiro C atom has been determined to be such that the methoxy group of ring *D* is oriented *syn* with respect to the H atom at the junction of rings *B* and *C*.

Introduction. Kreysiginone (dienone I), a minor alkaloid of *Kreysigia multiflora*, is a homoproaporphine alkaloid existing as one of the two possible spiro isomers (Battersby, McDonald, Munro & Ramage, 1967; Battersby, Bradbury, Hervert, Munro & Ramage, 1974). The stereostructures of these two isomers, dienone I and dienone II (Fig. 1), have been proposed on the basis of chemical reactivity towards hydrochloric acid (Kametani, Satoh, Yagi & Fukumoto, 1967, 1968). Apart from the natural product, dienone II has been synthesized from a phenolic 1-phenethyltetrahydroisoquinoline and the structure of its methiodide derivative has been determined by X-ray methods. A brief account of the stereospecific synthesis has been published along with a preliminary report of the present structure determination (Hara, Hoshino, Umezawa & Iitaka, 1977).

Diffraction data were obtained from a crystal of approximate dimensions 0·13 × 0·18 × 0·25 mm. The lattice constants were determined by the least-squares treatment of the setting angles of 23 reflexions measured on a Philips PW 1100 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The 2θ angles ranged from 21 to 35°.

Intensities were measured by the θ–2θ scan method at a scan speed of 6° min^{-1} in θ. When the total counts during the first scan were less than 3000, scans were repeated twice. The background was measured at each end of the scan for half the total scan time.

2852 reflexions were measured in a θ range of 3 ~ 23°; of these, 2767 reflexions with $I > 2\sigma(I)$ were used for the subsequent structure analysis. The intensities were corrected for Lorentz and polarization factors but not for absorption. The crystal structure was determined by the heavy-atom method. The locations of almost all the lighter atoms were found on the electron density map synthesized by using the phase angles of the calculated structure factors with the iodide ion. Refinement of the structural parameters was carried out by the block-diagonal least-squares method using the program *HBLS* (Okaya & Ashida, 1967). The atomic scattering factors of C, N, O and I$^-$ and the dispersion corrections of the iodine atom for Mo $K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1974). The following weighting system was adopted: $w^{1/2} = 0{\cdot}1$ for $F_o < 5$, $w^{1/2} = 5/|F_o|$ for $F_o > 5$. The final R value was 0·05. The atomic parameters are given in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33848 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The stereostructures of the dienone molecules are now established and illustrated in Figs. 1 and 2. The configuration at the spiro atom C(8a), which gives two spiro isomers in the dienone, has been determined to be such that the methoxy group at C(10) of ring *D* is oriented *syn* with respect to H(C6a) in dienone II.

Table 1. *Final atomic coordinates and their standard deviations*

The coordinates are multiplied by 10^5 for the iodide ion and by 10^4 for the other atoms.

	x	*y*	*z*
I	80431 (3)	6268 (4)	15157 (2)
C(1)	4960 (3)	3174 (5)	−8 (4)
C(2)	5141 (4)	3650 (6)	−504 (3)
C(3)	5835 (4)	3956 (6)	−369 (4)
C(3a)	6351 (3)	3794 (5)	286 (3)
C(4)	7109 (4)	4208 (7)	435 (4)
C(5)	7656 (3)	3911 (7)	1133 (4)
N(6)	7349 (3)	3988 (5)	1673 (3)
C(6a)	6769 (3)	3086 (6)	1510 (3)
C(7)	6469 (4)	2976 (7)	2051 (4)
C(8)	5923 (4)	2034 (6)	1799 (4)
C(8a)	5247 (3)	2394 (5)	1169 (3)
C(9)	4842 (3)	1299 (6)	891 (4)
C(10)	4244 (3)	1054 (6)	957 (4)
C(11)	3915 (3)	1814 (6)	1297 (3)
C(12)	4211 (4)	2936 (6)	1459 (4)
C(13)	4817 (4)	3195 (6)	1382 (4)
C(14)	5463 (3)	2976 (5)	639 (3)
C(15)	6191 (3)	3278 (5)	801 (3)
C(16)	3889 (4)	2155 (6)	−567 (4)
C(17)	3118 (4)	2124 (9)	−655 (5)
C(18)	4741 (5)	3602 (8)	−1724 (5)
C(19)	7070 (4)	5152 (6)	1702 (4)
C(20)	7952 (4)	3753 (7)	2357 (4)
C(21)	4090 (5)	−713 (7)	353 (6)
O(1)	4240 (2)	2987 (4)	−142 (2)
O(2)	4165 (3)	1547 (6)	−845 (3)
O(3)	4586 (3)	3880 (5)	−1145 (3)
O(4)	3404 (3)	1502 (5)	1413 (3)
O(5)	3861 (3)	60 (4)	742 (3)

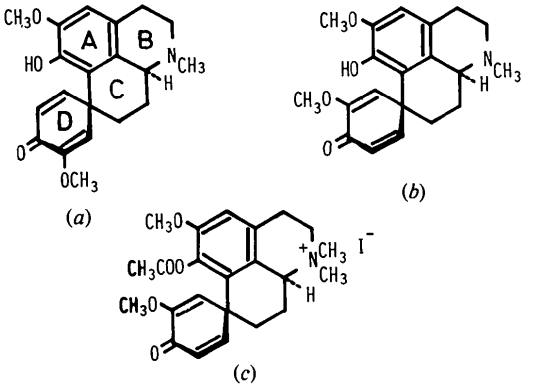

Fig. 1. Stereostructures of the dienones. (*a*) Dienone I (kreysiginone). (*b*) Dienone II. (*c*) Acetyl dienone II methiodide.

The bond lengths and bond angles are shown in Figs. 2 and 3 respectively. The mean estimated standard deviations of the C–C bond lengths and C–C–C angles are 0·010 Å and 0·6°, respectively, but larger values of up to 0·014 Å and 0·8° are expected for those involving the terminal atoms, O(2), C(17), C(18) and C(21). There are no anomalous bond lengths and angles found in the molecule but some are worth mentioning. The C(3a)–C(15) and C(14)–C(15) bonds involved in ring *A*, lying at the junctions of the saturated rings *B* and *C*, are slightly longer than the other four bonds in the benzene ring. In ring *D*, the C(9)–C(10) and C(12)–C(13) bonds are much shorter than the other bonds while C(8a)–C(9) and C(8a)–C(13) are longer indicating that the C(8a) atom does not participate in the conjugation of ring *D*.

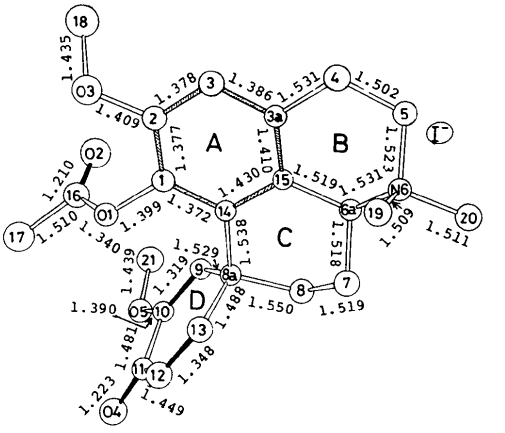

Fig. 2. Bond lengths (Å) found in the crystal of acetyl dienone II methiodide. Shaded bonds represent conjugated double bonds and black bonds represent double bonds.

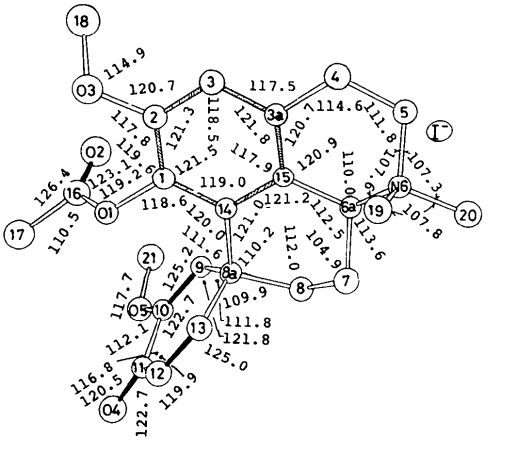

Fig. 3. Valency angles (°). The following angles are not shown: C(6a)–N(6)–I = 65·2, C(5)–N(6)–I = 68·6, C(19)–N(6)–I = 177·2, C(20)–N(6)–I = 74·8, C(6a)–N(6)–C(20) = 110·3, C(6a)–N(6)–C(19) = 112·5, C(5)–N(6)–C(19) = 111·3, C(8)–C(8a)–C(9) = 104·8, C(14)–C(8a)–C(13) = 108·5°.

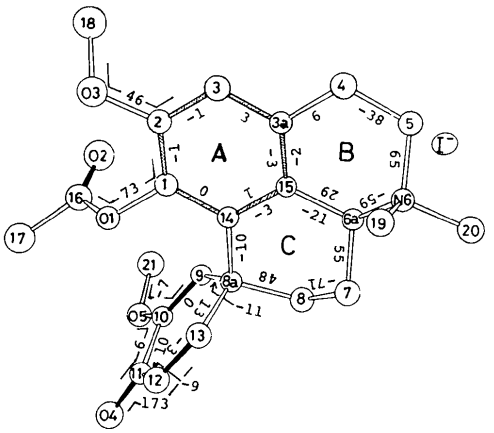

Fig. 4. Endocyclic and some other torsion angles (°).

The endocyclic torsion angles calculated for each ring are shown in Fig. 4 along with some other torsion angles demonstrating the orientations of the substituted groups. It is clear that rings *B* and *C* take a half-chair form with the poles at C(7) and N(6), while ring *D* distorts in a shallow boat form with flag poles at C(8a) and C(11). The planarities of each ring and the acetyl group are illustrated in Table 2 which also shows the conformation of the ring. The exocyclic methoxy groups are not coplanar with rings *A* and *D*. The torsion angle C(3)–C(2)–O(3)–C(18) is as much as 46·1° in ring *A* while the corresponding angle, C(9)–C(10)–O(5)–C(21), in ring *D* is only 7·1°. The acetyl group is also markedly twisted out from ring *A*, and the torsion angle C(2)–C(1)–O(1)–C(16) is 72·9°.

The authors are grateful for the financial support of this work by a grant-in-aid for Scientific Research (No. 067186) from the Ministry of Education. They are indebted to Professor A. R. Battersby of the University of Cambridge for the NMR and IR spectra of dienone II and to Professor T. Kametani of Tohoku University for the IR spectrε of kreysiginone and dienone II.

Table 2. *Deviations* (Å) *of atoms from the least-squares planes*

The atoms marked by asterisks are not included in the least-squares calculation.

Ring *A*		Ring *D*	
C(1)	0·008	C(8a)	0·089
C(2)	−0·003	C(9)	−0·043
C(3)	−0·010	C(10)	−0·040
C(3a)	0·017	C(11)	0·080
C(15)	−0·012	C(12)	−0·030
C(14)	−0·001	C(13)	−0·055
O(1)*	0·163	O(4)*	0·225
O(3)*	0·079	O(5)*	−0·102
		C(8)*	1·516
		C(14)*	−0·959

Ring *B*		Acetyl group	
C(3a)	−0·009	O(1)	0·003
C(4)	0·004	O(2)	0·004
C(6a)	−0·004	C(16)	−0·009
C(15)	0·009	C(17)	0·003
C(5)*	−0·106	C(1)*	0·032
N(6)*	0·667		

Ring *C*	
C(8a)	−0·006
C(14)	0·013
C(15)	−0·013
C(6a)	0·006
C(7)*	0·557
C(8)*	−0·300

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