Tetrahedron Letters No.30, pp. 2527-2530, 1969. Pergamon Press. Printed in Great Britain.

THE X-RAY ANALYSIS OF ONE RACEMIC STEREOISOMER OF DEACETYLASPIDOSPERMINE

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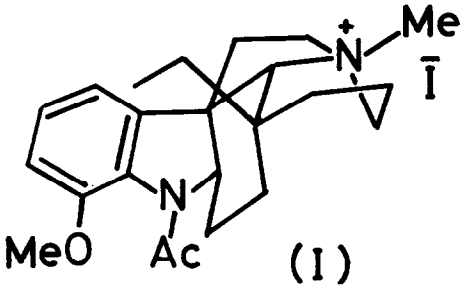
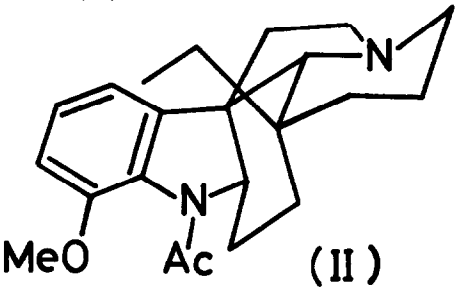
(Received in Japan 6 May 1969; received in UK for publication 23 May 1969)

The crystal structure of aspidospermine N(b)-methiodide was established as formula (I) by Mills and Nyberg (1) in terms of X-ray analysis. Based upon this result, Smith and Wrobel (2) suggested that ring D of aspidospermine ($C_{22}H_{30}N_2O_2$) itself constitutes a chair form, since it indicates a clear absorption in the region of 2750-2800 $cm.^{-1}$ (3). If the alkaloid had the same conformation as formula (I), no band in this region would be observed. Aspidospermine, therefore, has been represented by formula (II).



(I)



(II)

The racemic stereoisomer ($C_{20}H_{28}N_2O$), colorless prisms, m.p. 89.5-90.5°, of deacetylaspidospermine synthesized by Ban and Iijima (4), was converted to the corresponding N(a)-hydriodide ($C_{20}H_{28}N_2O$ HI), m.p. 245-246°, which was reconverted into the initial base without any stereochemical change observed with natural aspidospermine. Thus, the above salt was subjected to X-ray analysis.

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* The reprint request and inquiry of this paper should be addressed to Y. Ban.

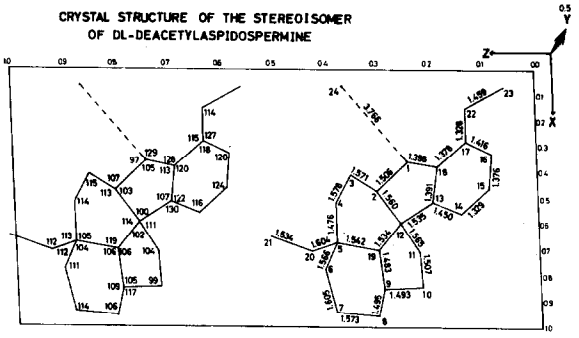
TABLE I

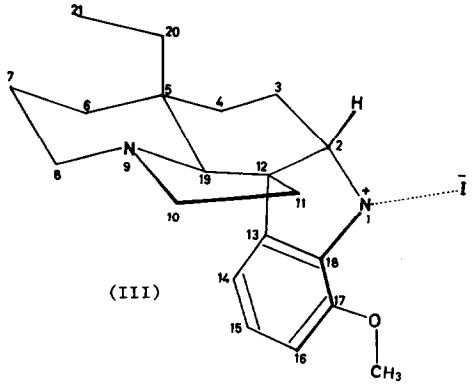
Final atomic co-ordinates and temperature factors.

Nr	Atom	X/a	Y/b	Z/c	B	Nr	Atom	X/a	Y/b	Z/c	B
1	N	.3538	.2836	.2464	3.309	13	C	.5100	.1467	.2000	3.226
2	C	.4691	.2581	.3054	3.447	14	C	.5555	.0606	.1484	3.471
3	C	.4041	.1656	.3574	4.966	15	C	.4590	.0353	.0944	3.619
4	C	.5164	.0712	.3875	3.844	16	C	.3221	.0841	.0865	3.897
5	C	.6707	.1076	.3874	3.430	17	C	.2776	.1694	.1361	3.417
6	C	.7764	.0057	.4104	4.793	18	C	.3745	.2010	.1923	3.260
7	C	.9408	.0356	.3910	4.831	19	C	.7002	.1286	.3069	3.441
8	C	.9572	.0778	.3107	4.499	20	C	.7039	.2217	.4354	3.027
9	N	.8495	.1741	.2980	3.619	21	C	.6497	.2125	.5125	5.103
10	C	.8439	.2308	.2251	3.956	22	C	.1512	.2259	.1338	3.256
11	C	.7048	.2991	.2310	3.961	23	C	.0599	.2060	.0678	4.856
12	C	.5968	.2087	.2620	2.904	24	I	.0644	.3919	.3674	4.009

* The (B)-column indicates temperature factors of output, and each temperature factor of input is put as 3.00. R-factor = 14.33%.

FIG. 1





(III)

The colorless crystals recrystallized from methanol are monoclinic with the unit cell of the dimensions, a=9.17, b=11.51, c=18.44 Å and β=93°, the space group being $P2_1/c$, and there are four melecules per unit cell. The observed crystal density, Do=1.512 $g.cm.^{-3}$, was almost same as the calculated one, Dc=1.504 $g.cm.^{-3}$.

Intensity data were collected with Cu-Kα radiation from equi-inclination Weissenberg photographs of the layers h0l— h7l and hk0— hk8 by applying the multiple film technique. The relative intensities of 3384 reflections were estimated visually by comparison with the standard charts and the relative values of the observed structure factors were converted into absolute scale by Wilson's method (5). In this stage were obtained co-ordinates of twenty four atoms. The whole structure was elucidated by successive application of the Fourier synthesis and the least-squares method. Final atomic co-ordinates and temperature factors are listed in TABLE I, and the crystal structure projected along the b axis are illustrated in FIG. 1 with bond lengths and bond angles. The R-factor calculated with all structure factors is 14.33%. Thus, the complete chemical formula of this compound is represented by formula (III).

As mentioned above, the crystal structure of aspidospermine N(b)-methiodide (I) analyzed by Mills and Nyberg (1) does not reflect the molecular structure of aspidospermine (II) in situ. It is noteworthy that the crystal structure analyzed in this work directly proves the actual stereochemistry of one racemic stereoisomer of deacetylaspidospermine itself.

The calculations were performed on the NEAC-2206 electronic computer, for which use the authors are indebted to Dr. Masao Nishikawa and Mr. Kazuhiko Kamiya, Takeda Chemical Industries, Ltd. The authors are grateful to Prof. Yoshimasa Hirata and Prof. Jiro Tanaka, Nagoya University, for much useful advice and many helpful discussions. This work was supported by the grant of National Institutes of Health, U. S. A.(5 RO 1 MH 08187), which is gratefully acknowledged.

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