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The Crystal Structure and the Absolute Configuration of (—)-Argemonine Methiodide

Tsuguhiro Kaneda, Noriyoshi Sakabe, and Jiro Tanaka
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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The crystal structure of (—)-argemonine methiodide has been investigated by the X-ray method. The crystal system is orthorhombic, and the space group is $P2_12_12_1$. The cell dimensions are $a=13.443$, $b=20.838$, and $c=8.485$ Å. The structure parameters were refined by the block-diagonal least-squares method, and the final R-value was 0.055. The absolute configuration was determined by the Mo$K\alpha$ anomalous scattering to be 1S5S, which is consistent with the CD result.

Argemonine is an alkaloid from *Argemone hispida G* and *Argemone munita*, and its structure was determined by Martell, Soine, and Kier[1] to be identical with (—)-*N*-methylpavine, which was synthesized by Battersby and Binks.[2] The absolute configurations of (—)-argemonine and its related alkaloids have been established by Barker and Battersby[3] by the chemical correlation method. Mason and his coworkers[4,5] have investigated the CD spectra of these molecules and further investigations on the conformation and the absolute configuration by the X-ray method will be of much interest.

In this paper we present a precise structure analysis of (—)-argemonine methiodide and its absolute configuration by the X-ray method.

Experimental

Argemonine methiodide was kindly gifted from Prof. T. O. Soine of Minnesota Univ., and it was recrystallized from water for the X-ray examination. The space group was determined from oscillation and Weissenberg photographs. The density was measured by the flotation method in a mixed solution of cyclohexane and carbon tetrachloride. The cell dimensions were determined by the least-squares method, using 12 reflections which had been carefully measured on a Hilger-Watts four circle diffractometer with Ni-filtered Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). The crystal data are shown in Table 1.

Table 1. Crystal data

M.F.: $C_{22}H_{28}NO_4I\cdot 2H_2O$
M.W.: 533.41
Crystal system: orthorhombic
Space group: $P2_12_12_1$
$a=13.443(2)$, $b=20.838(2)$, $c=8.485(2)$ Å;
$V=2376.9$ Å^3, $Z=4$,
$D_m=1.486$, $D_c=1.491$ g·cm^{-3}
$\mu=15.81$ cm^{-1} (for Mo$K\alpha$ radiation).

Intensity data were measured on the diffractometer in ω-2θ scanning mode using Zr-filtered Mo$K\alpha$ radiation ($\lambda=0.7107$ Å) with the crystal whose size was $0.5\times0.7\times0.8$ mm. Non-zero data of 2766 independent reflections within $\theta\leq26°$ were collected and no correction were made for absorption or extinction.

Structure analysis

The crystal structure was determined by the heavy atom method. Iodine atom was found from a Patterson map and a Fourier synthesis using the coordinate of the iodine atom revealed all the other non-hydrogen atoms including two water molecules of crystallization. A diagonal-least-squares method was applied to the refinement of structure parameters by using all non-zero data and the R-value was reduced to 0.098. Successively a block-diagonal least-squares method was applied to further refinement with anisotropic thermal factors for all atoms and the R-value was converged to 0.055. No other significant peaks were found in the final Fourier and difference Fourier maps. All atomic scattering factors were taken from the International Tables for X-ray Crystallography.[6] The computation was carried out with the program of HBLS-IV coded by Prof. Ashida

Table 2. Atomic coordinates and their standard deviations

	x	y	z
I	0.13050(6)	0.22007(4)	0.98752(9)
O(1)	0.4788(6)	0.4495(4)	0.7229(9)
O(2)	0.5317(6)	0.4585(3)	0.4340(9)
O(3)	0.6618(5)	0.0708(4)	0.2969(9)
O(4)	0.7034(8)	0.0714(4)	0.5914(9)
C(1)	0.3223(8)	0.2369(5)	0.6432(12)
C(2)	0.3749(7)	0.2966(4)	0.5722(10)
C(3)	0.4013(7)	0.3026(5)	0.4139(11)
C(4)	0.3721(9)	0.2519(4)	0.2928(11)
C(5)	0.3490(7)	0.1882(5)	0.3761(12)
C(6)	0.4420(6)	0.1589(4)	0.4458(11)
C(7)	0.4684(7)	0.1589(5)	0.6060(12)
C(8)	0.4003(8)	0.1941(5)	0.7266(12)
N(9)	0.2736(5)	0.1999(3)	0.5105(11)
C(10)	0.4020(8)	0.3457(4)	0.6829(12)
C(11)	0.4507(7)	0.3976(5)	0.6293(12)
C(12)	0.4786(7)	0.4036(4)	0.4684(12)
C(13)	0.4547(7)	0.3571(4)	0.3631(12)
C(14)	0.5084(7)	0.1286(4)	0.3360(12)
C(15)	0.5943(7)	0.1009(4)	0.3913(12)
C(16)	0.6171(7)	0.1015(4)	0.5531(11)
C(17)	0.5554(7)	0.1312(4)	0.6582(12)
C(18)	0.1841(7)	0.2392(5)	0.4519(14)
C(19)	0.2334(8)	0.1345(5)	0.5665(15)
C(20)	0.4621(10)	0.4427(6)	0.8886(12)
C(21)	0.5556(9)	0.4684(6)	0.2693(13)
C(22)	0.6520(9)	0.0778(6)	0.1308(13)
C(23)	0.7258(9)	0.0684(6)	0.7602(14)
OW(1)	0.6677(9)	0.5134(5)	0.6943(12)
OW(2)	0.7493(8)	0.5707(6)	0.4245(14)

TABLE 3. ANISOTROPIC THERMAL FACTORS ($\times 10^4$) AND THEIR STANDARD DEVIATIONS

The anisotropic thermal factors are of the form of $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	59(0)	28(0)	122(1)	−3(1)	11(1)	0(1)
O(1)	70(6)	21(2)	107(11)	−10(6)	−12(14)	−21(8)
O(2)	64(5)	18(2)	112(11)	−19(5)	−3(13)	7(7)
O(3)	61(5)	27(2)	115(11)	27(6)	19(13)	−17(9)
O(4)	42(4)	26(2)	124(11)	17(5)	−10(12)	6(9)
C(1)	43(6)	16(2)	105(14)	−5(6)	3(16)	9(9)
C(2)	34(5)	14(2)	105(12)	8(6)	0(15)	−2(8)
C(3)	38(5)	17(2)	97(13)	4(6)	−15(14)	−5(9)
C(4)	54(6)	16(2)	101(13)	−2(7)	−51(20)	−9(9)
C(5)	32(5)	17(2)	113(14)	0(6)	3(14)	9(10)
C(6)	32(5)	13(2)	95(13)	0(5)	1(13)	−12(9)
C(7)	36(5)	16(2)	96(14)	−6(6)	7(15)	7(10)
C(8)	51(6)	20(2)	92(14)	14(7)	42(16)	3(10)
N(9)	30(4)	17(2)	122(12)	−4(4)	24(15)	−10(10)
C(10)	50(6)	13(2)	101(14)	10(6)	21(15)	−11(9)
C(11)	41(5)	18(2)	100(14)	0(6)	−27(15)	−13(10)
C(12)	38(5)	14(2)	120(16)	−3(5)	−15(16)	19(10)
C(13)	40(5)	16(2)	99(14)	2(6)	−14(15)	2(10)
C(14)	39(5)	13(2)	119(15)	2(6)	17(16)	−13(10)
C(15)	41(5)	14(2)	114(15)	−1(6)	20(15)	−4(10)
C(16)	37(5)	15(2)	124(14)	1(6)	−3(15)	14(9)
C(17)	39(5)	15(2)	101(14)	0(6)	−4(15)	10(9)
C(18)	37(5)	27(3)	149(19)	15(7)	−7(17)	1(12)
C(19)	48(6)	20(3)	184(21)	−4(7)	35(20)	18(12)
C(20)	89(9)	24(3)	75(14)	10(9)	−12(20)	−18(11)
C(21)	64(7)	22(3)	107(15)	−5(8)	17(19)	29(11)
C(22)	65(8)	32(3)	103(15)	9(9)	49(19)	−6(13)
C(23)	50(7)	33(4)	117(16)	17(9)	−21(19)	5(14)
OW(1)	91(8)	45(4)	183(17)	−46(9)	−18(20)	−12(14)
OW(2)	116(10)	50(4)	245(22)	−62(11)	43(26)	−13(16)

and those written by ourselves on a FACOM 230-60 computer at Nagoya University Computation Center.

The atomic coordinates and the anisotropic thermal parameters with their standard deviations are listed in Tables 2 and 3, respectively. The observed and calculated structure factors are listed in Table 4.[7]

Results and discussion

Argemonine is a rigid molecule which has a bicyclo[3.3.1]nona-diene skeleton. Figure 1 shows the conformation and atomic labels, and thermal ellipsoids drawn by the program ORTEP coded by Dr. Johnson. The bond lengths and angles are shown in Tables 5 and 6, respectively. The average bond distance of dimethoxybenzene ring A {C(2), C(3), C(10), C(11), C(12), and C(13)} and that of dimethoxybenzene ring B {C(6) C(7), C(14), C(15), C(16), and C(17)} are 1.39 Å and

TABLE 5. BOND LENGTHS AND THEIR STANDARD DEVIATIONS

C(6)–C(7)	1.40(1) Å	C(2)–C(3)	1.39(1) Å
C(6)–C(14)	1.44(1)	C(2)–C(10)	1.44(1)
C(7)–C(17)	1.38(1)	C(3)–C(13)	1.41(1)
C(14)–C(15)	1.37(1)	C(10)–C(11)	1.34(1)
C(15)–C(16)	1.41(1)	C(11)–C(12)	1.42(1)
C(16)–C(17)	1.37(1)	C(12)–C(13)	1.36(1)
C(1)–C(2)	1.55(1)	C(5)–C(6)	1.51(1)
C(1)–C(8)	1.55(1)	C(4)–C(5)	1.54(1)
C(3)–C(4)	1.53(1)	C(7)–C(8)	1.56(1)
C(1)–N(9)	1.51(1)	C(5)–N(9)	1.55(1)
C(18)–N(9)	1.54(1)	C(19)–N(9)	1.54(1)
C(11)–O(1)	1.39(1)	C(15)–O(3)	1.36(1)
C(12)–O(2)	1.38(1)	C(16)–O(4)	1.36(1)
C(20)–O(1)	1.43(1)	C(22)–O(3)	1.42(1)
C(21)–O(2)	1.45(1)	C(23)–O(4)	1.46(1)

TABLE 6. BOND ANGLES AND THEIR STANDARD DEVIATIONS

C(2)–C(3)–C(13)	119.7(9)°	C(6)–C(7)–C(17)	121.7(9)°
C(2)–C(10)–C(11)	118.4(9)	C(6)–C(14)–C(15)	119.0(9)
C(3)–C(2)–C(10)	120.1(8)	C(7)–C(6)–C(14)	118.1(8)
C(3)–C(13)–C(12)	119.6(9)	C(7)–C(17)–C(16)	119.7(9)
C(10)–C(11)–C(12)	121.6(9)	C(14)–C(15)–C(16)	120.9(9)
C(11)–C(12)–C(13)	120.5(9)	C(15)–C(16)–C(17)	120.6(9)
C(1)–C(2)–C(10)	115.6(8)	C(5)–C(6)–C(14)	116.0(8)
C(4)–C(3)–C(13)	118.9(8)	C(8)–C(7)–C(17)	119.0(9)
C(5)–C(6)–C(7)	126.0(8)	C(1)–C(2)–C(3)	124.1(8)
C(6)–C(7)–C(8)	119.2(8)	C(2)–C(3)–C(4)	121.4(9)
C(2)–C(1)–C(8)	109.3(8)	C(4)–C(5)–C(6)	111.2(8)
C(3)–C(4)–C(5)	109.9(8)	C(1)–C(8)–C(7)	111.7(8)
C(2)–C(1)–N(9)	108.5(8)	C(6)–C(5)–N(9)	108.5(8)
C(8)–C(1)–N(9)	109.9(8)	C(4)–C(5)–N(9)	109.6(8)
C(10)–C(11)–O(1)	124.3(9)	C(14)–C(15)–O(3)	123.5(9)
C(12)–C(11)–O(1)	114.0(8)	C(16)–C(15)–O(3)	115.6(8)
C(11)–C(12)–O(2)	114.4(8)	C(15)–C(16)–O(4)	114.6(8)
C(13)–C(12)–O(2)	125.1(9)	C(17)–C(16)–O(4)	124.9(9)
C(11)–O(1)–C(20)	116.1(9)	C(15)–O(3)–C(22)	118.2(8)
C(12)–O(2)–C(21)	116.0(8)	C(16)–O(4)–C(23)	115.4(9)
C(1)–N(9)–C(18)	107.9(7)	C(5)–N(9)–C(19)	108.5(7)
C(1)–N(9)–C(19)	111.9(8)	C(5)–N(9)–C(18)	111.0(8)
C(1)–N(9)–C(5)	110.2(7)		
C(18)–N(9)–C(19)	107.2(7)		

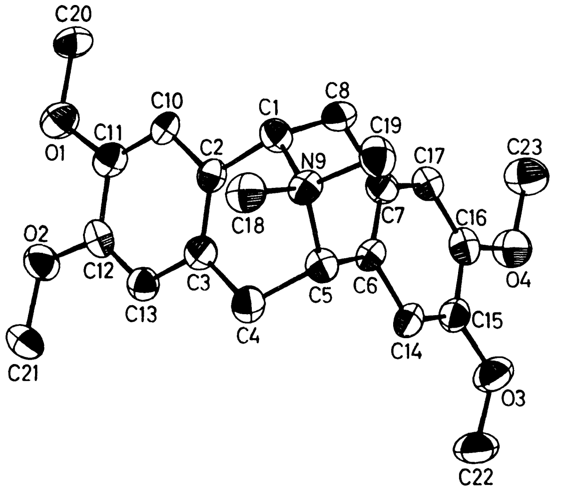

Fig. 1. The conformation and atomic labels. The atoms are represented as thermal ellipsoids of a size such that the center of the vibrating atoms have a 50% probability of being found within them.

1.40 Å, respectively. The distances of four methoxyl groups are normal. The C–C single bond distances at the part of the bicyclo ring are also normal with the average value of 1.54 Å.

The bond angles of two benzene rings are in the range of 120±2°. The external angles around C(2), C(3), C(6), and C(7) are 115.6—119.0°, while the internal angles of bicyclo site are 119.2—126.0°. These trends are noticed in triptycene derivatives which have a bicyclo[2.2.2]octatriene skeleton.[8)]

Intermolecular distances within 3.6 Å are listed in Table 7, and the closest contact of 3.29 Å occurs between O(3) and C(23) ($3/2-x$, $-y$, $-1/2+z$). Projection along the c axis is shown in Fig. 2. There is a hydrogen bond network including four hydrogen bonds around the screw axis.

Table 7. Intermolecular distances less than 3.6 Å[a)]

O(2) ·········C(19$^{\mathrm{i}}$)	3.33 Å
O(2) ·········C(22$^{\mathrm{ii}}$)	3.55
O(3) ·········C(23$^{\mathrm{iii}}$)	3.29
O(4) ·········C(20$^{\mathrm{iv}}$)	3.49
OW(1) ······C(19$^{\mathrm{iv}}$)	3.50
C(12)·········C(19$^{\mathrm{i}}$)	3.53
C(13)·········C(23$^{\mathrm{v}}$)	3.60
C(14)·········C(21$^{\mathrm{iv}}$)	3.56
C(16)·········C(18$^{\mathrm{i}}$)	3.44
C(16)·········C(20$^{\mathrm{iv}}$)	3.51
C(17)·········C(18$^{\mathrm{i}}$)	3.34
C(19)·········C(21$^{\mathrm{v}}$)	3.50
C(20)·········C(21$^{\mathrm{vi}}$)	3.50
C(22)·········C(23$^{\mathrm{vii}}$)	3.30

Symmetry code

Symmetry code superscript	Symmetry operator		
i	$1/2+x$	$1/2-y$	$1-z$
ii	$1-x$	$1/2+y$	$1/2-z$
iii	$3/2-x$	$-y$	$-1/2+z$
iv	$1-x$	$-1/2+y$	$3/2-z$
v	$-1/2+x$	$1/2-y$	$1-z$
vi	x	y	$1+z$
vii	x	y	$-1+z$

a) The Roman numerals represent the symmetry operators relevant to the atoms listed second.

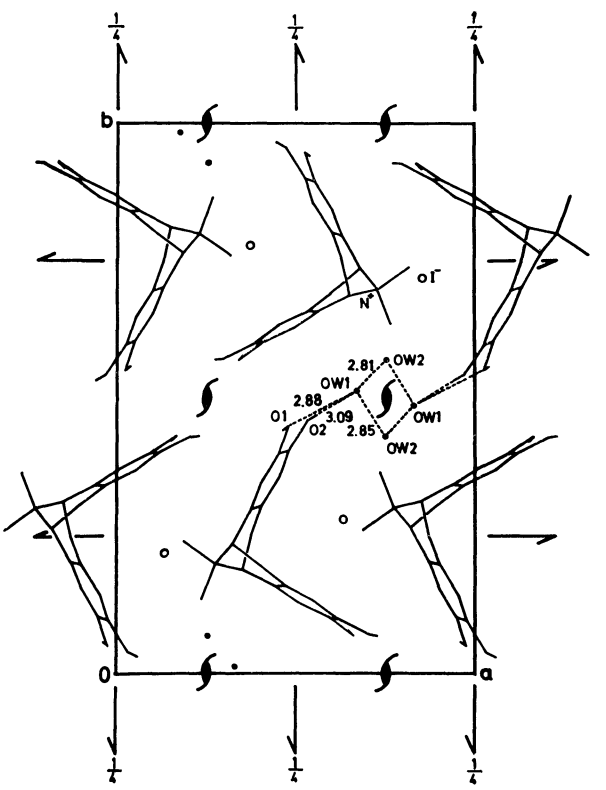

Fig. 2. Projection along the c axis.

The planarity of the benzene rings, A and B, is remarkably good. The least-squares planes of the two rings are given by the following equations.

(1) Ring A

$$0.8652X - 0.4652Y + 0.1869Z - 2.3957 = 0$$

(2) Ring B

$$0.4855X + 0.8650Y - 0.1267Z - 5.2726 = 0$$

Deviations of atoms from these planes are listed in Table 8. C(1) and C(4) deviate 0.08 and —0.05 Å from the A plane, respectively, and C(8) deviates 0.06 Å from

Table 8. Deviations from the least-squares plane

(1) Dimethoxybenzene-ring plane (A)			
C(2)	0.00 Å	C(1)*	0.08 Å
C(3)	−0.01	C(4)*	−0.05
C(10)	0.01	C(20)*	0.10
C(11)	−0.01	C(21)*	−0.05
C(12)	0.00	O(1)*	−0.04
C(13)	0.01	O(2)*	0.03
		N(9)*	−0.34
(2) Dimethoxybenzene-ring plane (B)			
C(6)	0.00 Å	C(5)*	−0.01 Å
C(7)	0.00	C(8)*	0.06
C(14)	0.00	C(22)*	0.24
C(15)	0.00	C(23)*	−0.12
C(16)	−0.01	O(3)*	0.00
C(17)	0.01	O(4)*	−0.03
		N(9)*	−0.43

* Atoms not included in the least-squares calculation.

TABLE 9. DETERMINATION OF ABSOLUTE CONFIGURATION

h	*k*	*l*	$100\times\{I(hkl)-I(\bar{h}\bar{k}\bar{l})\}/I(hkl)$	
			Obsd	Calcd
1	6	6	13.2	9.4
1	6	7	−12.0	−13.2
1	15	2	−11.6	−12.4
2	5	7	4.3	9.8
2	7	7	−8.6	−10.2
3	5	6	−7.1	−11.9
3	7	2	15.4	12.8
3	10	5	6.1	11.2
4	2	1	−10.7	−10.7
4	2	6	−5.8	−11.0
4	6	3	11.3	14.6
5	2	7	−8.3	−10.2
5	3	1	−14.3	−14.9
5	3	8	8.2	10.0
6	4	2	−5.1	−10.3
7	2	3	−5.7	−10.3
7	2	5	15.6	13.0
7	4	3	8.4	9.4
8	3	4	−5.2	−10.1
8	4	1	6.1	10.4
9	5	1	13.3	9.2
11	9	2	−10.8	−9.7

the B plane. The methoxyl carbons, C(22) and C(23), which are attached to oxygen atoms not taking part in hydrogen bonding, deviate 0.24 and −0.12 Å from the B plane, respectively, while C(20) and C(21) do not deviate from the A plane so much. The dihedral angle between A and B planes is 90.4°.

The absolute configuration was determined by the Bijvoet method using the anomalous scattering of Mo$K\alpha$ radiation by the iodine atom. The $\Delta f'$ and $\Delta f''$ values were taken from the International Tables for X-ray Crystallography.[6] The observed intensity differences and calculated ones between 22 Bijvoet pairs are listed in Table 9. The signs of observed values are in good agreement with those calculated based on the positional paramenters of Table 2 in the right-handed coordinate system. The absolute configuration thus determined is 1S5S as is illustrated in Fig. 1. This result is in perfect agreement with those by the chemical correlation method of Barker and Battersby,[3] and by the CD spectral analysis of Mason *et al.*[4,5] The structural data will be still useful for the theoretical calculation of the CD spectra.

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