Chem. Pharm. Bull. 13(6) 643~651 (1965)

UDC 547.94.02 : 582.757 : 545.824

84. Sataro Imado, Motoo Shiro,*1 and Zen-ichi Horii*2 : The Crystal Structure of Securinine Hydrobromide Dihydrate and the Molecular Structure of Securinine.*3

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Elaborate investigations have been made by the several authors on the physical and chemical properties of securinine, $C_{13}H_{15}O_2N$, an alkaloid which can be isolated from *Securinega suffruticosa* REHD. Thus, the chemical structure of this compound has been already determined, and its absolute configuration also has been established, as is shown in Fig. 1, mainly on the basis of the ORD curve and so on.

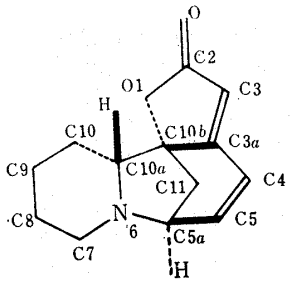

Fig. 1. Absolute Configuration of Securinine

In their reports, it was proposed that the lone electron pair on the nitrogen atom should exert a possibly strong influence on the diene part which probably would not lie on a plane,[1] as evidenced, *e.g.*, by the disappearance of absorption band (λ_{max} 330 mμ) in acidifying the alcoholic solution of securinine. However, no direct knowledges have been given yet regarding the steric configuration of the diene part itself. It is also the case with the piperidine ring.[2,3]

The present work was undertaken to confirm the chemical structure of securinine, and furthermore, to obtain exact and detailed conformational informations on this alkaloid molecule by means of X-ray crystal structure analysis.

Experimental

In order that the heavy atom method could be applied in analyzing procedures, the hydrobromide of securinine was prepared. Needle-like and colorless crystals of the anhydrous, mono- and di-hydrated compounds were obtained from ethanol solutions; their crystallographic data are given in Table I, and the results of elemental analyses in Table II.

TABLE I. Crystallographic Data of Securinine·HBr·nH$_2$O

n	a(Å)	b(Å)	c(Å)[a]	γ(°)	Space group	Z[b]	$\rho_{obs.}$	$\rho_{calc.}$ (g. cm^{-3}.)
2	7.71	14.83	7.04	112.13	C_2^2-$P2_1$	2	1.492	1.488
1	9.64	21.80	6.55		D_2^4-$P2_12_12_1$	4		1.510
0	12.31	14.17	7.23		D_2^4-$P2_12_12_1$	4	1.572	1.570

a) The *c*-axis lies along a direction of elongation of the needle-like crystals.
b) Number of formula units per unit cell.

Of those, however, the crystal of dihydrated compound was found to be most stable, showing the dehydrating range of 110~120°, and the melting point of about 250°(decomp.). Therefore, the present work was conducted on the dihydrated compound.

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*3 S. Imado, M. Shiro, Z. Horii : Chem. & Ind. (London), **1964**, 1691.

1) Z. Horii, M. Ikeda, Y. Tamura, S. Saito, M. Suzuki, K. Kotera : This Bulletin. **12**, 1118 (1964).
2) S. Saito, K. Kotera, A. Shigematsu, A. Ide, N. Sugimoto, Z. Horii, M. Hanaoka, Y. Yamawaki, Y. Tamura : Tetrahedron, **19** (12), 2085 (1963).
3) Z. Horii, M. Ikeda, Y. Yamawaki, Y. Tamura, S. Saito, K. Kotera : *Ibid.*, **19** (12), 2101 (1963).

Table II. Results of Chemical Analyses

	n		C(%)	N(%)	H(%)	Br(%)
$C_{13}H_{15}O_2N \cdot HBr \cdot nH_2O$	2	found	46.60	4.44	5.71	23.70
		calcd.	46.72	4.19	6.03	23.91
	1	found	49.31		5.75	
		calcd.	49.38		5.74	
	0	found	50.41	4.60	5.25	25.94
		calcd.	52.36	4.70	5.41	26.80

The unit cell dimensions and the space group were determined (Table I) from the oscillation and Weissenberg photographs taken with Cu Kα radiation about the three principal axes.

For the intensity measurments, the reflections of ($hk0$) to ($hk5$) were recorded on equi-inclination Weissenberg photographs, employing the multiple film technique. The specimen used was a small needle-like crystal of about 0.1×0.2 mm. cross section. Visual estimations of the intensities were made for the 1416 observed reflections in the usual way, and they were corrected for the spot-size (for upper layers) and Lorentz-polarization factors. No absorption corrections were applied.

Because of the shape of the crystals, reliable data were prevented from being obtained about the a- and b-axes; the analysis was made mainly on the basis of the ($hk0$) to ($hk5$) data, and the less reliable ($0kl$) data about the a-axis was used as a check on the essential correctness of the atom locations as will be described below.

Structure Determination

The structure was determined by making use of the heavy atom method. The x- and y-coordinates of the bromine atom were derived from the Patterson function, P (UV). With the signs given by the contributions of the bromine atom, the electron density projection, ρ (XY), was evaluated. There showed up the peaks corresponding to all of the light atoms, and consequently, refinements for the x- and y-coordinates of all atoms were made successively following the conventional Fourier technique. Finally, the value of R for ($hk0$) came to 0.180.

On the other hand, the determination of z-parameters was forced to be carried out without uses of the projections along the a- and b-axes owing to the heavy overlappings of the atoms in the Fourier maps. Then, z-parameters of the light atoms were assigned relatively to z-parameter of the bromine atom, $z=0.0000$, since the choice of it in space group $P2_1$ (for 1st setting) is arbitrary. With ($hk1$) data, the generalized components R_1 (XY) and I_1 (XY)[4] were computed, and the z-parameters were adjusted by using the relation, $2\pi Lz_i = \tan^{-1} I_L(X_iY_i)/R_L(X_iY_i)$. In those projections the other parameters of each atom were also refined. The same procedure was put forward with ($hk5$) data. After several refinements, the R indices for ($hk0$), ($hk1$) and ($hk5$) were reduced to 0.143, 0.111, and 0.127, respectively.

The structure was then refined by the method of least squares. At first the refinements were separately carried out in each layer of ($hk1$) to ($hk5$). The block-diagonal approximations were applied for the scale factor and the overall isotropic temperature factor as well as for the positional parameters of each atom. After the scale factors had been fixed the data of different layers were correlated, and then the structure was improved by the same program, as the above using all the data of ($hk1$) to ($hk5$). The weighting system employed was as follows:

$$\sqrt{w} = 0 \quad \text{for} \quad F_o > 30\,F_{min.}$$
$$\sqrt{w} = 1/|F_o| \quad \text{for} \quad 2.2\,F_{min.} \leq F_o \leq 30\,F_{min.}$$
$$\sqrt{w} = 0 \quad \text{for} \quad F_o < 2.2\,F_{min.}$$

4) These denotements are used as in M. J. Buerger: "Crystal-Structure Analysis," 392 (1960), John Wiley & Sons, Inc., New York, London.

and the 908 of 1162 terms were meaningful. The atomic structure factors were calculated with the aid of the analytical representations given by Vand, *et al.*[5] The final set of atomic coordinates is shown in Table Ⅲ, and their standard deviations in Table Ⅳ, the temperature factor B being 3.3 Å^2 for all atoms. The R values for (*hk*0), (*hk*1), (*hk*2), (*hk*3), (*hk*4), and (*hk*5) were 0.135, 0.105, 0.105, 0.106, 0.090, and 0.115, respectively, with the exception of the terms too weak to be observed. Observed and calculated structure factors are listed in Table Ⅴ. The contributions of hydrogen atoms were neglected.

Table Ⅲ. Atomic Coordinates Expressed in Fraction of Unit Cell Edges

Atom[a]	x	y	z	Atom[a]	x	y	z
Br	0.3950	0.2114	0.9963	C 4	0.4396	0.4295	0.5401
C 7	0.0056	0.1173	0.5936	C 5	0.4313	0.3379	0.4828
C 8	0.8997	0.0777	0.7805	C 3	0.2351	0.5311	0.5443
C 9	0.8294	0.1561	0.8845	C 2	0.0288	0.5009	0.5203
C 10	0.8504	0.2393	0.7449	N 6	0.1407	0.2182	0.6259
C 10*a*	0.0541	0.2912	0.6893	O	0.9362	0.5496	0.5271
C 5*a*	0.2458	0.2650	0.4453	O 1	0.9499	0.4013	0.5089
C 11	0.1144	0.3033	0.3503	O (H_2O)	0.6035	0.1126	0.3254
C 10*b*	0.0890	0.3623	0.5068	O (H_2O)	0.3837	0.0530	0.6482
C 3*a*	0.2721	0.4509	0.5377				

a) The atoms are numbered as in Fig. 1.

Table Ⅳ. Averaged Standard Deviations of Atomic Coordinates in Å

Atom	σ(x)	σ(y)	σ(z)	Atom	σ(x)	σ(y)	σ(z)
Br	0.0016	0.0016	0.0062	N	0.021	0.021	0.022
C	0.023	0.023	0.026	O	0.015	0.015	0.017

At this stage, the evaluation of the electron density projection along the a-axis (Fig. 2) was attempted to see the appropriateness of the structure obtained with the c-axis data; for the atomic arrangement given in Table Ⅲ the R index for the (0*kl*) was found to be 0.131. Thus it was confirmed that the structure model based on the c-axis data was reasonably fitted.

The absolute configuration of securinine hydrobromide was established on the basis of the Bijvoet's inequality relation due to the anomalous dispersion of bromine atom. The intensities of (*hk*l) and (*hk*$\bar{\text{l}}$) reflections were visually compared with one another on the oscillation photographs taken about the c-axis (Table Ⅵ). The absolute configuration, thus determined, is correctly indicated by the atomic parameters in Table Ⅲ. The right-handed coordinate system was used throughout this work. The indexing of the reflexions followed the work of Peerdeman, *et al.*[6] This method has been applied in the determination of the absolute configuration of securinine hydrobromide dihydrate.

Description of Structure

Packing of the molecules: The arrangement of the molecules is shown in Figs. 2 and 3. In these figures, the broken and dot-dash lines represent the hydrogen bond and the close approaches, respectively.

5) V. Vand, P.F. Eiland, R. Pepinsky: Acta Cryst., **10**, 303 (1957).
6) A.F. Peerdeman, J.M. Bijvoet: Acta Cryst., **9**, 1012 (1956).

TABLE V. Observed and Calculated Structure Factors (×10)

	F_o	F_c
h 0 0		
1	110	108
2	398	436
3	153	212
4	382	366
5	257	268
6	224	200
7	33	24
8	31	46
0 k 0		
1	-	214
2	373	448
3	508	562
4	255	296
5	180	210
6	254	236
7	348	330
8	104	134
9	273	264
10	137	118
11	91	90
12	177	180
13	36	4
14	91	102
15	7	30
16	47	48
1 k 0		
1	960	960
2	336	430
3	507	496
4	42	32
5	570	552
6	275	226
7	116	118
8	318	262
9	85	88
10	126	136
11	21	12
12	42	66
13	162	156
14	37	32
15	53	64
-1	123	148
-2	73	158
-3	174	228
-4	241	316
-5	91	104
-6	263	318
-7	430	456
-8	52	10
-9	350	356
-10	50	56
-11	126	164
-12	129	124
-13	105	90
-14	50	86
-15	24	10
-16	50	74
-17	10	8
2 k 0		
1	348	364
2	365	298
3	114	136
4	493	404
5	203	224
6	340	370
7	36	8
8	145	146
9	80	56
10	183	162
11	30	22
12	68	78
13	58	78
14	15	2
-1	490	554
-2	241	284
-3	180	198
-4	150	198
-5	258	256
-6	526	640
-7	122	178
-8	131	148
-9	190	220
-10	56	28
-11	102	106
-12	52	72
-13	7	40
-14	114	114
-15	91	100
-16	50	60
-17	22	26
-18	58	58
3 k 0		
1	375	422
2	123	104
3	134	142
4	172	218
5	62	74
6	218	222
7	208	218
8	156	152
9	55	84
10	15	12
11	98	90
12	21	26
13	58	62
-1	483	492
-2	46	86
-3	375	414
-4	214	294
-5	163	176
-6	223	288
-7	236	252
-8	310	322
-9	85	72
-10	249	278
-11	123	108
-12	125	160
-13	300	270
-14	21	12
-15	110	120
-16	16	14
-17	37	50
-18	6	22
4 k 0		
1	120	142
2	312	296
3	39	14
4	162	136
5	142	138
6	212	198
7	129	150
8	15	26
9	156	136
10	13	4
11	52	56
12	6	40
-1	326	372
-2	332	334
-3	150	184
-4	45	4
-5	297	346
-6	251	254
-7	409	416
-8	214	230
-9	43	28
-10	217	236
-11	58	88
-12	187	196
-13	46	10
-14	39	52
-15	65	70
-16	7	10
-17	47	48
-18	25	16
5 k 0		
1	80	86
2	98	96
3	186	162
4	56	48
5	96	98
6	74	68
7	108	96
8	13	14
9	33	32
10	45	50
-1	150	176
-2	234	226
-3	230	218
-4	162	116
-5	200	188
-6	194	182
-7	197	202
-8	25	14
-9	234	226
-10	99	120
-11	223	240
-12	40	40
-13	74	76
-14	126	112
-15	19	26
-16	49	50
-17	18	28
-18	61	44
6 k 0		
1	34	42
2	53	30
3	114	102
4	7	4
5	68	86
6	36	50
7	47	30
8	76	64
9	4	16
-1	145	124
-2	199	168
-3	139	98
-4	101	108
-5	7	18
-6	191	204
-7	135	142
-8	7	0
-9	154	148
-10	15	20
-11	15	22
-12	82	78
-13	88	88
-14	59	68
-15	7	6
-16	68	58
-17	30	16
7 k 0		
1	134	130
2	7	6
3	126	94
4	55	52
5	31	26
6	61	64
-1	141	114
-2	49	74
-3	71	86
-4	141	114
-5	33	34
-6	184	176
-7	45	38
-8	116	76
-9	129	116
-10	71	52
-11	123	108
-12	49	60
-13	67	66
-14	30	26
-15	68	54
-16	39	40
8 k 0		
1	6	6
2	71	60
3	4	2
-1	102	92
-2	7	4
-3	131	88
-4	7	10
-5	82	72
-6	53	60
-7	40	32
-8	102	90
-9	7	16
-10	77	70
-11	31	28
-12	67	74
-13	79	62
-14	6	6
-15	70	60
9 k 0		
-1	31	26
-2	76	46
-3	55	50
-4	25	12
-5	73	62
-6	6	12
-7	40	38
-8	49	40
-9	37	34
-10	70	40
-11	30	18
-12	67	54
h 0 1		
1	165	166
2	585	615
3	414	409
4	34	23
5	80	59
6	203	176
7	89	82
8	77	58
9	21	22
0 k 1		
1	-	290
2	573	571
3	559	540
4	665	610
5	248	245
6	325	325
7	282	199
8	315	304
9	89	88
10	49	65
11	137	149
12	68	70
13	77	105
14	30	11
15	77	70
16	49	51
17	19	20
1 k 1		
1	414	406
2	551	524
3	278	264
4	293	270
5	329	287
6	515	422
7	159	152
8	98	111
9	249	230
10	45	62
11	245	225
12	39	31
13	49	66
14	45	51
15	34	35
16	13	37
-1	818	818
-2	105	119
-3	651	702
-4	229	249
-5	280	305
-6	398	387
-7	385	361
-8	194	197
-9	28	34
-10	312	280
-11	159	157
-12	156	159
-13	99	108
-14	15	28
-15	92	94
-16	12	1
-17	43	44
2 k 1		
1	334	298
2	805	681
3	79	92
4	393	312
5	125	127
6	42	43
7	380	303
8	85	69
9	139	138
10	107	135
11	40	55
12	110	112
13	56	42
14	55	58
15	4	10
-1	359	371
-2	584	603
-3	695	712
-4	113	119
-5	529	538
-6	221	197
-7	321	341
-8	107	86
-9	180	189
-10	261	252
-11	92	75
-12	138	154
-13	56	46
-14	172	154
-15	7	19
-16	13	25
-17	49	57
-18	21	13
3 k 1		
1	119	103
2	188	210
3	571	520
4	135	100
5	324	279
6	56	43
7	95	76
8	153	137
9	82	72
10	99	104
11	13	15
12	76	78
13	25	29
14	4	21
-1	267	222
-2	212	204
-3	211	204
-4	460	445
-5	232	246
-6	367	352
-7	177	204
-8	110	110
-9	297	302
-10	65	73
-11	96	89
-12	181	191
-13	93	108
-14	33	34
-15	49	34
-16	83	89
-17	45	44
-18	56	46
4 k 1		
1	393	340
2	86	99
3	229	217
4	119	99
5	110	106
6	129	130
7	120	109
8	55	60
9	33	35
10	104	94
11	36	37
12	39	31
13	22	37
-1	153	122
-2	321	315
-3	141	136
-4	422	418
-5	163	157
-6	224	253
-7	181	184
-8	160	178
-9	172	173
-10	43	56
-11	157	148
-12	98	109
-13	56	84
-14	113	96
-15	67	71
-16	64	76
-17	12	12
-18	28	39
5 k 1		
1	267	229
2	58	77
3	141	146
4	188	185
5	79	62
6	98	104
7	47	55
8	89	79
9	42	48
10	34	22
11	10	34
-1	190	177
-2	36	22
-3	252	251
-4	147	164
-5	47	43
-6	301	284
-7	13	17
-8	188	168
-9	74	58
-10	71	71
-11	188	169
-12	49	57
-13	175	180
-14	31	35
-15	86	97
-16	58	52
-17	37	37
-18	67	46
6 k 1		
1	88	94
2	197	160
3	28	16
4	86	91
5	85	64
6	104	69
7	34	44
8	31	24
9	53	62
-1	45	44
-2	39	39
-3	221	178
-4	110	107
-5	310	261
-6	47	40
-7	91	62
-8	221	223
-9	91	109
-10	197	152
-11	74	86
-12	137	126
-13	56	57
-14	39	45
-15	64	66
-16	25	22
-17	76	54
-18	4	5
7 k 1		
1	42	48
2	102	85
3	58	54
4	37	21
5	79	58
6	28	17
7	15	34
-1	55	46
-2	114	100
-3	163	149
-4	129	103
-5	95	79
-6	58	78
-7	180	156
-8	15	23
-9	108	98
-10	73	75
-11	56	58
-12	111	80
-13	7	18
8 k 1		
1	50	38
2	80	49
3	15	29
4	9	12
-1	45	22
-2	62	53
-3	7	9
-4	86	61
-5	99	82
-6	116	98
-7	96	72
-8	19	21
-9	117	94
-10	27	26
-11	67	46
-12	50	44
-13	13	17
-14	65	52
-15	19	16
9 k 1		
-1	53	43
-2	47	31
-3	25	18
-4	114	77
-5	19	8
-6	104	48
-7	34	31
-8	82	50
-9	56	44
-10	36	23
-11	64	39
-12	43	27
-13	68	42
h 0 2		
1	277	283
2	244	244
3	254	254
4	92	83
5	212	202
6	186	149
7	7	7
8	6	15
0 k 2		
1	-	560
2	266	261
3	487	418
4	239	253
5	564	479
6	71	76
7	319	267
8	98	101
9	203	204
10	91	94
11	42	48
12	132	130
13	21	28
14	61	80
15	43	46
16	33	46
1 k 2		
1	627	712
2	512	510
3	376	374
4	65	49
5	387	350
6	125	128
7	246	213
8	370	327
9	153	128
10	150	155
11	21	23
12	45	48
13	34	49
14	86	68
15	18	43
-1	274	259
-2	835	739
-3	131	106
-4	531	531
-5	70	91
-6	211	224
-7	206	206
-8	116	106
-9	251	256
-10	74	85
-11	79	95
-12	114	112
-13	125	108
-14	61	92
-15	7	6

	F_o	F_c
-16	71	73
-17	12	17

2 k 2

1	317	294
2	108	108
3	317	317
4	364	315
5	197	160
6	212	185
7	95	74
8	108	130
9	104	84
10	159	149
11	50	74
12	19	20
13	73	69
14	6	11
15	36	43
-1	567	571
-2	131	136
-3	275	283
-4	329	361
-5	220	205
-6	236	242
-7	169	164
-8	177	188
-9	278	260
-10	104	122
-11	301	284
-12	39	28
-13	76	77
-14	95	96
-15	79	88
-16	40	49
-17	30	24
-18	45	54

3 k 2

1	351	367
2	264	215
3	53	65
4	326	298
5	134	127
6	239	199
7	138	135
8	243	206
9	67	89
10	25	28
11	77	73
12	6	15
13	53	58
14	3	19
-1	364	359
-2	163	170
-3	279	294
-4	178	161
-5	223	222
-6	217	193
-7	76	65
-8	407	386
-9	50	46
-10	196	222
-11	36	47
-12	21	36
-13	132	111
-14	36	34
-15	76	87
-16	33	24
-17	33	43
-18	19	28

4 k 2

1	134	115
2	260	240
3	30	39
4	145	134
5	194	189
6	70	63
7	79	85
8	45	33
9	120	108
10	22	26
11	43	48
12	15	34
-1	289	267
-2	257	258
-3	243	254
-4	64	72
-5	316	326
-6	196	206
-7	315	293
-8	99	117
-9	58	65
-10	230	236
-11	46	39
-12	196	160
-13	21	26
-14	61	65
-15	74	78
-16	49	49
-17	61	61
-18	4	10

5 k 2

1	95	79
2	154	142
3	159	149
4	98	78
5	88	97
6	21	34
7	141	116
8	16	31
9	28	34
10	43	42
-1	16	30
-2	263	233
-3	98	110
-4	212	174
-5	178	168
-6	108	108
-7	154	146
-8	93	95
-9	177	166
-10	139	144
-11	174	163
-12	21	26
-13	21	19
-14	119	106
-15	13	24
-16	28	43
-17	47	46
-18	13	5

6 k 2

1	21	22
2	30	34
3	139	114
4	30	40
5	91	80
6	22	33
7	43	34
8	33	47
-1	126	132
-2	227	190
-3	65	57
-4	191	191
-5	150	135
-6	150	131
-7	151	120
-8	126	103
-9	172	159
-10	76	76
-11	96	101
-12	79	72
-13	92	83
-14	56	49
-15	15	15
-16	70	63

7 k 2

1	139	116
2	24	33
3	47	43
4	39	43
5	12	10
6	49	50
-1	147	112
-2	46	59
-3	98	93
-4	98	79
-5	74	39
-6	125	114
-7	15	17
-8	93	72
-9	92	84
-10	33	34
-11	108	94
-12	7	8
-13	59	49
-14	55	42
-15	65	52
-16	46	37

8 k 2

1	36	29
2	61	55
3	19	13
-1	107	82
-2	22	21
-3	142	94
-4	13	22
-5	73	56
-6	73	47
-7	24	28
-8	108	77
-9	7	7
-10	122	92
-11	50	48
-12	76	49
-13	56	40
-14	27	16
-15	36	33

9 k 2

-1	34	24
-2	36	31
-3	40	37
-4	33	16
-5	61	54
-6	18	13
-7	47	36
-8	67	53
-9	28	25
-10	70	45
-11	4	5
-12	45	44

h 0 3

1	282	270
2	114	112
3	374	377
4	34	29
5	77	76
6	129	110
7	71	67
8	56	45

0 k 3

1	443	434
2	480	421
3	450	349
4	246	222
5	290	255
6	202	173
7	110	92
8	273	239
9	108	110
10	134	137
11	188	192
12	42	42
13	108	124
14	7	9
15	27	37
16	4	15

1 k 3

1	120	126
2	539	512
3	80	91
4	312	285
5	209	194
6	368	334
7	116	121
8	13	10
9	119	111
10	30	29
11	126	148
12	18	31
13	61	68
14	67	72
15	24	16
-1	428	439
-2	49	38
-3	144	147
-4	65	85
-5	284	321
-6	327	329
-7	257	264
-8	236	249
-9	37	33
-10	172	155
-11	21	40
-12	116	117
-13	21	34
-14	24	28
-15	53	55
-16	6	7
-17	30	37

2 k 3

1	104	93
2	309	315
3	34	38
4	220	232
5	203	187
6	76	52
7	321	288
8	39	37
9	86	68
10	21	39
11	47	63
12	70	78
13	24	25
14	25	43
-1	224	244
-2	102	119
-3	259	281
-4	202	205
-5	380	414
-6	47	43
-7	313	313
-8	114	105
-9	59	56
-10	91	85
-11	21	40
-12	68	102
-13	92	75
-14	92	107
-15	15	36
-16	10	21
-17	39	47

3 k 3

1	175	170
2	95	80
3	178	160
4	175	168
5	172	192
6	77	52
7	108	97
8	116	132
9	49	35
10	80	76
11	21	15
12	56	63
13	15	5
-1	125	130
-2	331	326
-3	141	154
-4	292	317
-5	211	221
-6	174	186
-7	188	201
-8	122	124
-9	120	113
-10	91	73
-11	92	90
-12	160	171
-13	107	111
-14	70	89
-15	40	33
-16	65	55
-17	22	25

4 k 3

1	321	309
2	39	15
3	211	191
4	45	39
5	168	154
6	135	130
7	79	79
8	50	61
9	27	35
10	49	61
11	16	33
-1	183	189
-2	236	246
-3	61	59
-4	275	258
-5	30	27
-6	163	155
-7	193	187
-8	150	149
-9	154	139
-10	85	103
-11	148	162
-12	15	25
-13	91	106
-14	86	87
-15	43	39
-16	39	39
-17	25	12

5 k 3

1	162	148
2	159	152
3	21	23
4	107	109
5	28	41
6	91	75
7	16	26
8	89	64
9	34	33
10	31	29
-1	215	196
-2	104	110
-3	135	115
-4	110	89
-5	93	83
-6	246	243
-7	111	94
-8	180	185
-9	25	31
-10	50	54
-11	98	97
-12	15	17
-13	116	115
-14	7	7
-15	46	43
-16	28	22
-17	39	35

6 k 3

1	68	71
2	125	108
3	47	26
4	52	72
5	47	45
6	37	36
7	25	40
8	9	6
-1	61	73
-2	21	17
-3	123	98
-4	46	41
-5	187	183
-6	73	76
-7	30	40
-8	131	142
-9	21	32
-10	86	73
-11	58	60
-12	110	93
-13	71	59
-14	42	40
-15	64	56
-16	9	16

7 k 3

1	22	20
2	79	63
3	27	24
4	53	42
5	39	44
-1	43	47
-2	59	56
-3	83	75
-4	85	86
-5	85	66
-6	45	50
-7	203	163
-8	77	73
-9	73	45
-10	99	73
-11	42	35
-12	82	68
-13	6	4
-14	67	60
-15	28	27

8 k 3

1	43	42
2	34	32
-1	37	32
-2	88	72
-3	36	13
-4	82	51
-5	105	77
-6	82	63
-7	82	64
-8	33	22
-9	79	57
-10	6	15
-11	73	53
-12	36	30
-13	33	26
-14	74	50

9 k 3

-3	12	5
-4	46	44
-5	13	13
-6	64	41
-7	9	16
-8	55	41
-9	30	31
-10	15	22

h 0 4

1	183	145
2	150	154
3	131	119
4	120	102
5	113	101
6	122	114
7	6	9
8	4	6

0 k 4

1	226	226
2	255	251
3	214	208
4	181	178
5	306	264
6	52	63
7	217	220
8	34	43
9	131	150
10	71	77
11	31	23
12	42	58
13	7	9
14	47	60
15	15	24

1 k 4

1	285	258
2	290	288
3	211	214
4	95	94
5	153	131
6	104	100
7	116	109
8	137	142
9	104	104
10	93	109
11	13	7
12	37	47
13	49	45
14	37	40
-1	88	84
-2	370	392
-3	77	67
-4	289	289
-5	199	198
-6	52	34
-7	171	158
-8	18	21
-9	190	187
-10	42	44
-11	95	99
-12	111	109
-13	52	53
-14	55	68
-15	10	10
-16	52	56

2 k 4

1	261	257
2	62	76
3	261	246
4	191	175
5	203	161
6	190	174
7	79	71
8	148	168
9	93	88
10	129	114
11	40	61
12	37	26
13	25	39
-1	425	418
-2	142	143
-3	217	221
-4	217	217
-5	27	25
-6	206	204
-7	27	39
-8	169	185
-9	137	152
-10	113	111
-11	154	161
-12	49	51
-13	67	77
-14	49	51
-15	53	60
-16	45	48

3 k 4

1	187	212
2	150	142
3	31	33
4	187	192
5	64	78
6	80	82
7	56	70
8	88	94
9	22	40
10	6	13
11	61	60
12	18	23
-1	157	149
-2	71	69
-3	248	265
-4	125	169
-5	128	123
-6	172	180
-7	13	29
-8	232	245
-9	45	61
-10	148	167
-11	56	62
-12	28	20
-13	74	74
-14	30	27
-15	58	61
-16	16	9

4 k 4

1	53	56
2	162	183
3	62	64
4	93	82
5	102	115
6	64	68
7	79	83
8	15	20
9	99	88
10	12	14
11	13	28
-1	159	162
-2	145	143
-3	126	129
-4	18	15
-5	135	141
-6	59	56
-7	160	162
-8	71	86
-9	70	65
-10	120	122
-11	46	26
-12	104	93

	Fo	Fc
-13	16	18
-14	9	29
-15	64	72
-16	4	7

5 k 4

1	31	33
2	95	108
3	77	79
4	74	61
5	50	58
6	7	12
7	61	66
8	16	29
9	24	28
-1	36	25
-2	177	187
-3	107	105
-4	154	171
-5	177	184
-6	24	15
-7	129	115
-8	92	86
-9	122	122
-10	138	143
-11	101	105
-12	52	52
-13	43	44
-14	91	79
-15	6	23
-16	55	48

6 k 4

1	88	89
2	46	32
3	129	109
4	28	34
5	79	57
6	31	24
7	25	25

	Fo	Fc
-1	88	88
-2	128	126
-3	56	48
-4	89	87
-5	47	54
-6	95	72
-7	92	78
-8	73	59
-9	122	118
-10	27	26
-11	77	77
-12	40	42
-13	64	57
-14	30	35
-15	10	13

7 k 4

1	59	57
2	10	20
3	31	37
4	25	35
-1	86	67
-2	31	36
-3	71	69
-4	116	103
-5	31	21
-6	110	84
-7	7	12
-8	86	74
-9	39	37
-10	71	60
-11	76	77
-12	25	13
-13	45	38
-14	22	19

8 k 4

-1	50	47
-2	4	7
-3	77	59

	Fo	Fc
-4	6	14
-5	40	39
-6	24	30
-7	10	13
-8	39	45
-9	16	20
-10	40	41
-11	39	31
-12	22	21

h 0 5

1	169	159
2	186	184
3	160	169
4	79	85
5	59	46
6	76	78
7	56	48

0 k 5

1	200	158
2	206	186
3	230	178
4	203	175
5	132	138
6	172	165
7	64	67
8	187	171
9	73	87
10	77	81
11	80	89
12	21	20
13	58	66
14	25	12

1 k 5

1	145	131
2	177	146
3	39	46
4	203	200

	Fo	Fc
5	98	91
6	196	202
7	85	74
8	16	17
9	126	110
10	39	22
11	105	92
12	28	28
13	55	46
-1	237	236
-2	135	144
-3	283	299
-4	119	135
-5	159	170
-6	147	165
-7	79	76
-8	93	80
-9	16	8
-10	76	85
-11	43	40
-12	93	85
-13	42	51
-14	16	24
-15	58	58

2 k 5

1	113	97
2	251	233
3	98	85
4	147	144
5	92	86
6	67	50
7	139	147
8	22	19
9	70	70
10	36	55
11	7	25
12	55	53
-1	99	112
-2	107	71

	Fo	Fc
-3	148	140
-4	70	58
-5	145	150
-6	62	62
-7	151	165
-8	96	85
-9	107	98
-10	132	130
-11	9	21
-12	88	90
-13	46	44
-14	80	71
-15	9	22

3 k 5

1	98	99
2	73	78
3	162	166
4	22	24
5	111	126
6	9	14
7	58	53
8	64	58
9	70	67
10	58	65
11	30	16
-1	15	32
-2	188	200
-3	119	127
-4	156	161
-5	174	197
-6	93	93
-7	125	129
-8	43	40
-9	113	128
-10	46	59
-11	71	73
-12	92	98
-13	43	36
-14	43	41

	Fo	Fc
-15	52	27

4 k 5

1	159	156
2	42	39
3	126	145
4	28	48
5	80	78
6	98	100
7	28	25
8	62	56
9	30	26
-1	91	91
-2	135	135
-3	70	59
-4	180	173
-5	50	58
-6	128	139
-7	110	125
-8	86	98
-9	101	111
-10	9	13
-11	59	76
-12	7	14
-13	77	68
-14	62	60
-15	71	54

5 k 5

1	92	84
2	76	71
3	77	68
4	85	83
5	24	24
6	46	46
7	36	31
-1	110	111
-2	9	17
-3	110	113
-4	85	95

	Fo	Fc
-5	28	38
-6	131	154
-7	24	23
-8	85	101
-9	28	35
-10	58	70
-11	64	84
-12	21	27
-13	79	75
-14	18	11
-15	22	34

6 k 5

1	21	24
2	80	69
3	22	23
4	46	44
5	21	21
-1	56	49
-2	9	13
-3	104	95
-4	50	61
-5	119	115
-6	31	40
-7	49	53
-8	65	73
-9	21	28
-10	15	53
-11	7	5
-12	46	60
-13	39	32
-14	30	29

7 k 5

1	12	22
2	46	51
-1	30	28
-2	67	56
-3	50	59
-4	52	55

	Fo	Fc
-5	64	60
-6	12	17
-7	85	85
-8	22	18
-9	50	51
-10	64	61
-11	4	4
-12	67	60

8 k 5

-3	7	12
-4	25	23
-5	46	46
-6	43	45
-7	52	43
-8	7	8
-9	52	52

TABLE VI. Comparison of the Observed Inequality with Calculated Values

h	k	l	I $(hkl)^{a)}$	I $(hk\bar{l})$	observed$^{b)}$	h	k	l	I $(hkl)^{a)}$	I $(hk\bar{l})$	observed$^{b)}$
5	1	1	618	596	?	3	$\bar{7}$	1	822	908	<
5	2	1	64	48	>	4	$\bar{7}$	1	398	446	<
5	3	1	181	191	?	4	$\bar{9}$	1	258	274	?
8	6	1	88	73	>	4	$\bar{11}$	1	203	162	>

a) Calculated relative intensity, $\Delta f'=0.9$ and $\Delta f''=+1.5$ being used for bromine atom.

b) The inequality sign > shows that the observed intensity for (hkl) is larger than that for $(hk\bar{l})$, and the symbol ? that the inequality could not be decided.

Securinine molecules are linked through N-H...Br...H-O to a spiral chain, which is composed of the hydrogen-bonded water molecules and extend along the two-fold screw axis (Figs. 2 and 3). Hence, the crystal can be considered to be made up of hydrogen-bonded layers of the securinine molecules and crystal water, running parallel to (110). A water molecule is hydrogen-bonded to two water molecules and a bromine atom with the approximately tetrahedral angles (105°, 108°, 111°; 107, 115°, 121°). On the other hand, a bromine atom is linked to a nitrogen atom and two water molecules through the hydrogen bonds with the similar angles (104°, 110, 114°). Thus, the arrangement of the three carbon and bromine atoms is approximately tetrahedral around the nitrogene atom. It may be suggested that the lone electron pair on the nitrogen atom even in the free base might be located substantialy along the direction of N...Br as shown in the present work. This situation is in good agreement with the findings obtained by spectral measurements.[1)]

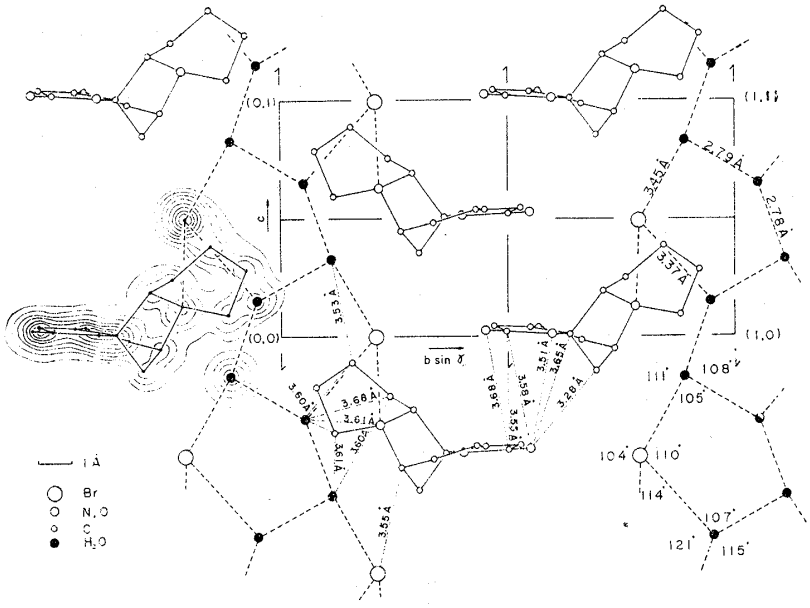

Fig. 2. The Structure and the Electron-density Projection along the *a*-Axis, with Bond Angles and Intermolecular Distances

Contours are at every 2 e. Å^{-2}, starting at two electron level, except around the bromine atom.

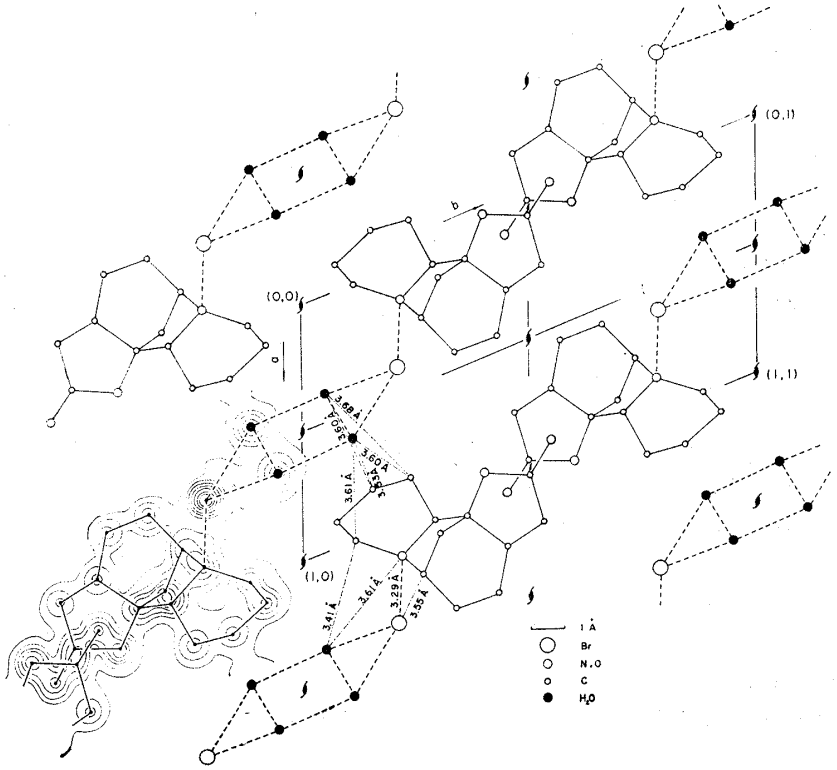

Fig. 3. The Structure and the Electron-density Projection along the *c*-Axis, with Intermolecular Distances

Contours are at every 2 e. Å^{-2}, starting at two electron level, except around the bromine atom.

Molecular structure of securinine : The bond lengths and bond angles, calculated by the use of the parameters in Table Ⅲ, are given in Fig. 4. The standard deviations of bond lengths and angles were estimated to be about 0.03 Å and 2°, respectively.

The three C-N bonds and the Br-N bond are arranged approximately tetrahedrally around the nitrogen atom (C-N-C : 103°, 112°, 115°; C-N-Br : 107°, 115°, 117°).

The skeleton of securinine molecule is shown Fig. 5, being oriented in accord with its absolute configuration. It can be seen easily that the piperidine ring has the "boat" form, and that the α, β and γ, δ-unsaturated lactone linkage is not co-planar. The C3=C3*a* bond and the C4=C5 bond in the diene part are not on a plane; in other words, one plane involving C2-, C3-, C3*a*-, C10*b*-, O- and O1-atoms is inclined to the plane which is composed of C3*a*-, C4-, C5-, C5*a*-, and C10*b*-atoms, the dihedral angle being about 10°.

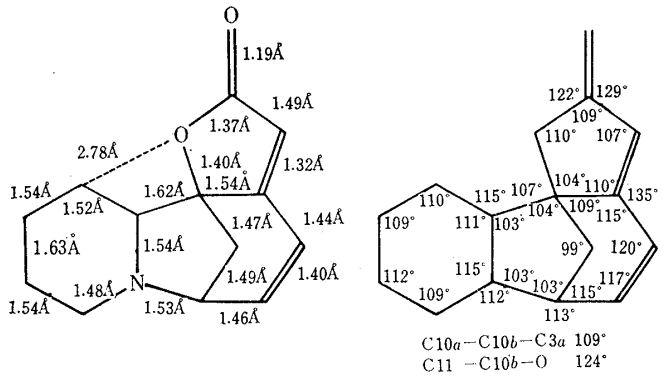

Fig. 4. Bond Distances and Bond Angles

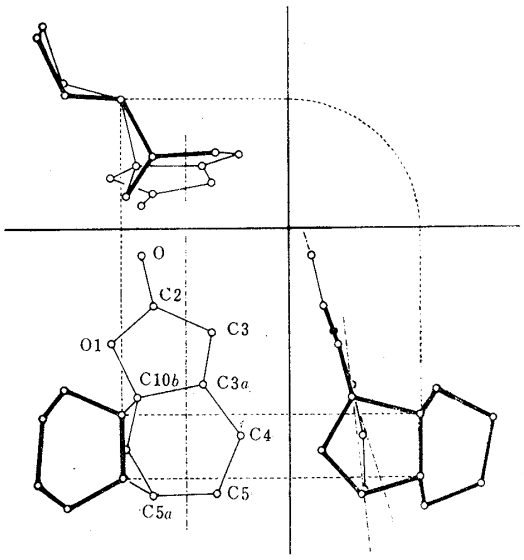

Fig. 5. Molecular Skeleton of Securinine in the Hydrobromide Dihydrate Crystal showing the Absolute Configuration

Table Ⅶ. Distances of Atoms from the Best Plane

(i) Best plane through C 10*b*, C 3*a*, C 3, C 2, O 1, O :
$-0.0651\,x - 0.0981\,y + 0.9920\,z - 3.1576 = 0$

Distances from plane :

C 10*b*	0.022Å	C 2	0.033Å
C 3*a*	−0.016Å	C 1	−0.025Å
C 3	−0.001Å	O	−0.013Å

(ii) Best plane through C 10*b*, C 3*a*, C 4, C 5, C 5*a* :
$0.0100\,x - 0.2608\,y + 0.9651\,z - 2.0951 = 0$

Distances from plane :

C 10*b*	−0.038Å	C 5	0.010Å
C 3*a*	0.059Å	C 5*a*	0.015Å
C 4	−0.047Å		

(iii) Angle between planes : about 10°
Coordinate system : $x = ax + b\cos\gamma$, $y = b\sin\gamma$, $z = cz$

The authors wish to express their sincere thanks to Prof. A. Shimada, Assist. Prof. K. Nakatsu and Dr. S. Ohi who have given the authors many invaluable suggestions, and Prof. H. Kuroya, who has shown his interest in this study and critically read the manuscript.

They thank also Prof. Y. Komiyama and the members of Electronic Data Processing Centre, Tanabe Seiyaku Co., Ltd. for the kind advices given in the course of the electronic computer programming.

Summary

X-ray crystal structure analysis has been made on the securinine hydrobromide dihydrate, which is monoclinic, with two formula units in a cell of dimensions : $a=7.71$ Å, $b=14.83$ Å, $C=7.04$ Å, and $\gamma=112.13°$. The space group is $P2_1$. The determination of the atomic parameters was carried out by the generalized projection methods.

The conclusions may be summed up as follows :

The piperidine ring has a skewed boat form, and the diene part is not co-planar. A dihedral angle of about 10° has been found between the plane passing through C2-, C3-, and C3*a*-atoms and the one involving C3*a*-, C4-, and C5-atoms.

Discussion has been made on the location of the lone electron pair on the nitrogen atom in the free base.

(Received December 31, 1964)

[Chem. Pharm. Bull. 13(6) 651~662 (1965)] UDC 547.682.1.07

85. Zen-ichi Horii, Takefumi Momose, and Yasumitsu Tamura : Synthetic Studies on η-Pyrromycinone II.*1 Synthesis of Methyl 2-Ethyl-5-hydroxy-1-naphthoate.

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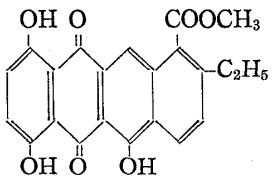
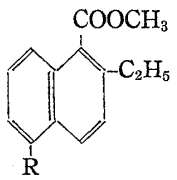
In recent communications,[1,2] the synthesis of η-pyrromycinone (I) has been accomplished *via* the Friedel-Crafts reaction of 3,6-dimethoxyphthalic anhydride and methyl 2-ethyl-5-hydroxy-1-naphthoate (II, R=OH). This paper describes a detail of the experiments for the synthesis of II (R=OH), which was carried out by a similar series of reactions to those for II (R=H) reported in the preceding paper.*1 The stereochemistries of the intermediate tetralone derivatives are also discussed.



I



II

Condensation of (*m*-methoxyphenyl)acetonitrile[3] with ethyl 2-pentenoate[4] in the presence of one molar equivalent of sodium ethoxide gave ethyl 3-ethyl-4-cyano-4-(*m*-methoxyphenyl)butyrate (III) in 65% yield. A short time alkaline hydrolysis of III gave three products, *i.e.* 3-ethyl-4-cyano-4-(*m*-methoxyphenyl)butyric acid (IV), 3-ethyl-4-carbamoyl-4-(*m*-methoxyphenyl)butyric acid (V) and 2-(*m*-methoxyphenyl)-3-ethylglutaric acid (VI). Refluxing III with 28% aqueous potassium hydroxide for 24 hours gave

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4) R. Tschesche, H. Barkemeyer, G. Heuschkel : Chem. Ber., **88**, 1258 (1955).