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X-RAY STRUCTURE DETERMINATION OF YUZURIMINE HYDROBROMIDE

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Five new types of alkaloids isolated from Daphniphyllum macropodum Miquel were reported in the previous papers (1) and (2). These five alkaloids may be classified into two groups, i.e. daphniphylline (1), neodaphniphylline (1) and codaphniphylline (2) are assigned to one group and yuzurimine (1) and neoyuzurimine (2) to a second group, since many differences are observed in their spectral data.

The structure of daphniphylline of the first group was determined by X-ray diffraction studies (3), and it was found that the carbon skeleton was very novel [Fig. 5]. We considered it valuable to elucidate the structure of yuzurimine hydrobromide by the X-ray analysis as a representative of the second group.

Yuzurimine hydrobromide, being crystallized from methanol, forms colorless plates, m.p. 251-253°C (dec. in a sealed tube), having a molecular formula $C_{27}H_{37}O_7N\cdot HBr$ (Found: C, 57.23; H, 6.76; N, 2.87 % Calcd.: C,57.04; H, 6.74; N, 2.46 %). It exhibits no UV absorptions (end, $\varepsilon = 7400$) and is a monoacidic base (pKa' 8.6). The spectral data of yuzurimine hydrobromide are as follows; $\nu_{max.}^{KBr}$ 3440, 2940, 1733, 1377, 1246, 1040 cm^{-1}; M/e 487 (M^{+}- HBr), 469, 410, 334; and NMR of the hydrochloride (Fig. 1 100 Mc. in $CDCl_3$). The NMR spectrum suggests that yuzurimine has two acetyl groups (1.98 ppm), a methoxyl group (3.53 ppm), a secondary methyl group (1.11 ppm) and a hydroxyl group (6.66 ppm) which disappeared when deuterium oxide was added. The presence of a double bond in the compound was suggested by the UV (end absorption, ε = 7400) spectrum.

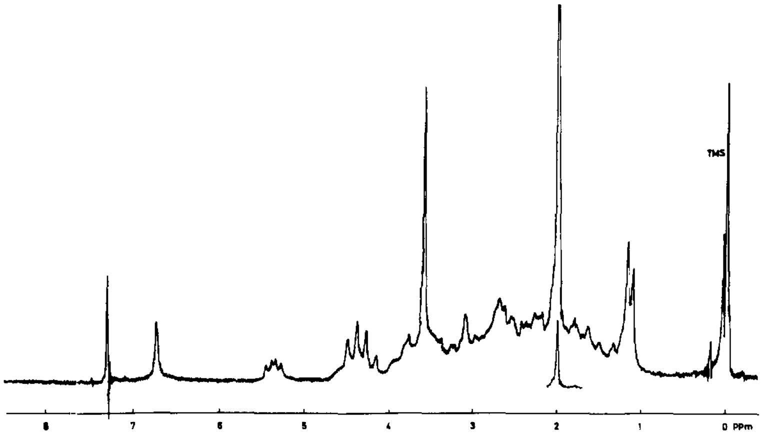


Fig. 1 NMR spectrum of yuzurimine hydrochloride solution in $CDCl_3$ at 100 Mc., ppm from internal TMS.

Crystal data were: $C_{27}H_{37}O_7N \cdot HBr$, M = 568.53; monoclinic; a = 8.67 ± 0.02, b = 9.51 ± 0.02, c = 15.92 ± 0.02 A, β = 99.5° ± 0.5° V = 1294 A^3; Dm = 1.41 $g \cdot cm^{-3}$; Dc = 1.45 $g \cdot cm^{-3}$; Z = 2; space group $P2_1$.

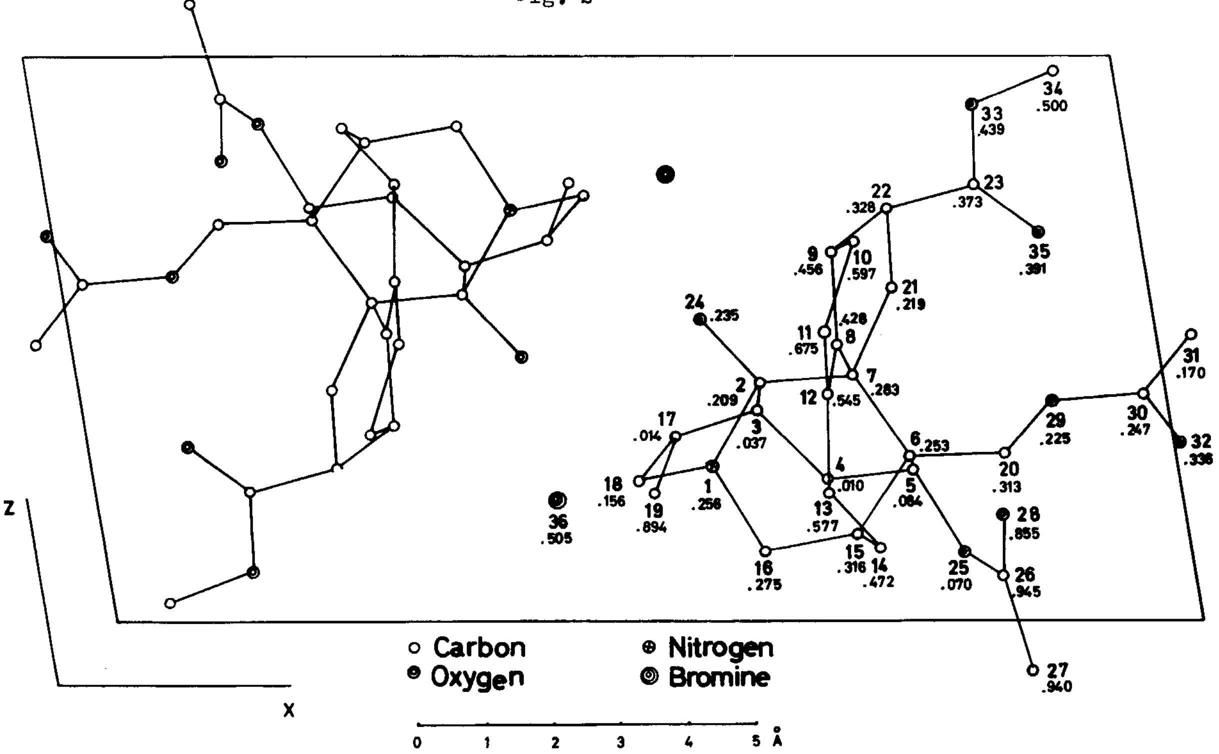
Intensity data were taken with Cu Kα radiation from equi-inclination Weissenberg photographs of layers h0l-h4l and hk0-hk4 by using multiple film technique. The relative intensities were estimated visually by comparing with a standard scale and relative values of the observed structure factors of independent 2159 reflections were converted into absolute scale by Wilson's method (4).

The co-ordinates of the bromine atoms were determined without ambiguity from a three-dimensional Patterson synthesis. Using the co-ordinates of the bromine atoms, the three-dimensional minimum function method was used for obtaining the positions of light atoms. Co-ordinates of seventeen atoms were obtained in this stage. The whole structure was elucidated by successive application of the Fourier syntheses and the least squares method. Final atomic co-ordinates and temperature factors are listed in Table 1, and the crystal structure projected along the b axis is illustrated in Fig. 2. Bond lengths shown in Fig. 3 and bond angles are all reasonable within estimated errors. The R factor calculated with all structure factors is 18.1 per cent.

Table 1, atomic co-ordinates and temperature factors of an yuzurimine hydrobromide crystal.

Atom		x/a	y/b	z/c	B	Atom		x/a	y/b	z/c	B
1	N	.5715	.2555	.2704	4.21	19	C	.5123	.8941	.2211	5.16
2	C	.6321	.2085	.4156	5.17	20	C	.8412	.3127	.2967	4.90
3	C	.6215	.0368	.3743	4.86	21	C	.7675	.2191	.5901	3.99
4	C	.6778	.0099	.2478	4.95	22	C	.7703	.3284	.7226	4.90
5	C	.7592	.0835	.2683	4.87	23	C	.8551	.3729	.7711	7.19
6	C	.7576	.2525	.2866	4.73	24	0	.5856	.2350	.5375	4.55
7	C	.7165	.2828	.4384	3.34	25	0	.7906	.0695	.1145	5.23
8	C	.7092	.4281	.4774	4.61	26	C	.8219	.9453	.0777	7.36
9	C	.7122	.4555	.6493	4.79	27	C	.8330	.9400	.9075	6.09
10	C	.7349	.5969	.6679	6.90	28	0	.8313	.8554	.1830	7.99
11	C	.6950	.6746	.5089	5.22	29	0	.9024	.2248	.3902	5.84
12	C	.6917	.5448	.3939	4.97	30	C	.9808	.2470	.4026	6.02
13	C	.6766	.5766	.2201	6.34	31	C	.0375	.1700	.5025	7.29
14	C	.7148	.4720	.1189	4.54	32	0	.0034	.3364	.3171	10.56
15	C	.6996	.3157	.1466	4.41	33	0	.8680	.4392	.9098	7.48
16	C	.6068	.2748	.1182	5.16	34	C	.9514	.5003	.9625	11.16
17	C	.5441	.0144	.3271	3.79	35	0	.9079	.3913	.6920	10.36
18	C	.4989	.1561	.2495	5.44	36	Br	.4265	.5047	.2098	5.70

Fig. 2


34 .500
33 .439
23 .373
22 .328
35 .391
9 .456
10 .597
21 .219
24 .235
11 .675
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7 .283
2 .209
12 .545
31 .170
17 .014
3 .037
6 .253
29 .225
30 .247
32 .336
18 .156
1 .256
4 .010
20 .313
19 .894
13 .577
5 .084
28 .855
36 .505
15 .316
14 .472
16 .275
25 .070
26 .945
27 .940
Z
X
Carbon
Oxygen
Nitrogen
Bromine
0
1
2
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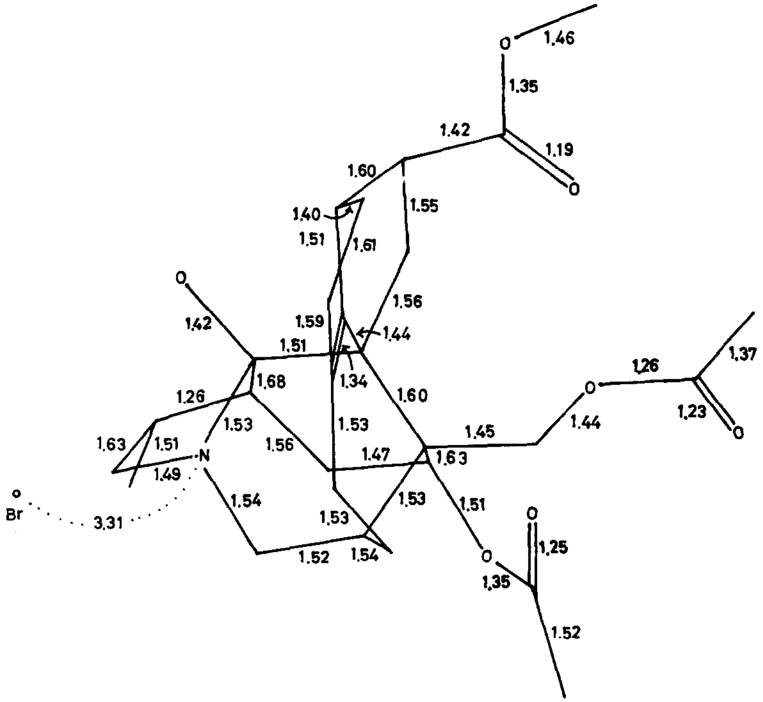

Fig. 3, bond lengths of yuzurimine hydrobromide

The complete chemical formula of yuzurimine hydrobromide is shown in Fig. 4. The skeleton of daphniphylline (Fig. 5) can be transformed into that of yuzurimine by the following formal procedures; bond formation from C_{18} to N_1 and from C_9 to C_{22}, bond fission between N_1 and C_{12}.

The calculations were performed using the NEAC-2206 electronic computer using our programs.

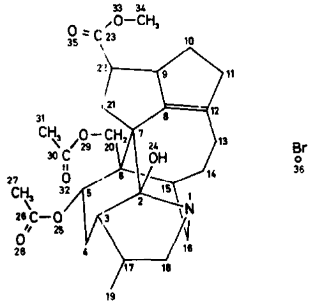

Fig. 4, the complete chemical formula of yuzurimine hydrobromide.

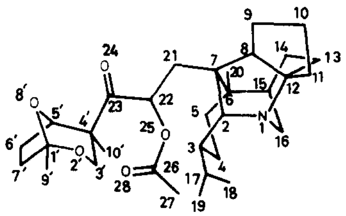

Fig. 5, the complete chemical formula of daphniphylline.

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