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X-RAY STRUCTURE DETERMINATION OF A NEW TYPE ALKALOID, DAPHNIPHYLLINE HYDROBROMIDE

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As discussed in the preceding paper (1), daphniphylline hydrochloride ($C_{32}H_{49}O_5N \cdot HCl$) was isolated from the Daphniphyllum macropodum Miquel. In order to transform the hydrochloride into the hydrobromide, an aqueous solution of sodium bicarbonate was dropped into an aqueous solution of daphniphylline hydrochloride, then free alkaloid was precipitated. After the precipitate was washed with water, it was crystallized from benzene containing a small amount of n-hexane and hydrogen bromide. Recrystallization was performed with the solvent mixture of benzene and n-hexane (5:1).

Crystals of the daphniphylline hydrobromide from benzene-n-hexane solution are monoclinic and belong to space group $P2_1$. The unit cell of dimensions a=19.477 A., b=9.423 A., c=10.031 A. and β=97° contains two molecules of the alkaloid and two molecules of benzene. Intensity data were collected with Cu Ka radiation from equi-inclination Weissenberg photographs of the layers hOl→h6l (2816 reflections) and hk0→hk5 (2218 reflections) by the multiple-film technique. Relative intensities were estimated visually by comparison with standard charts. These relative values were converted into absolute scale by Wilson's method (2).

Co-ordinate of the bromine atom was derived from the three-dimensional Patterson functions. For the solution of the co-ordinates of the light atoms, three-dimensional minimum function method

Table 1.

Atom		x/a	y/b	z/c	B	Atom		x/a	y/b	z/c	B
	Br	.4369	.2546	.0704	5.93	23	C	.8390	.9695	.8241	5.09
1	N	.5964	.2538	.0436	4.12	24	O	.8424	.0331	.7217	6.89
2	C	.6399	.1971	.9352	3.56	25	O	.7113	.9704	.7857	4.74
3	C	.6242	.2716	.8013	4.55	26	C	.7050	.8465	.7236	5.90
4	C	.6565	.4186	.7911	5.22	27	C	.6416	.8319	.6184	7.06
5	C	.7253	.4439	.8990	5.59	28	O	.7510	.7583	.7506	6.10
6	C	.7300	.3669	.0292	5.23	1'	C	.9286	.9564	.1626	6.67
7	C	.7124	.2089	.0103	4.17	2'	O	.8729	.8578	.1237	5.73
8	C	.7056	.1329	.1464	5.54	3'	C	.8771	.7782	.0101	5.97
9	C	.7030	.9641	.1459	5.34	4'	C	.8964	.8747	.8869	4.85
10	C	.6496	.9442	.2532	6.05	5'	C	.9539	.9726	.9426	5.45
11	C	.5913	.0438	.2028	5.72	6'	C	.0150	.8976	.0328	6.90
12	C	.6305	.1776	.1762	4.93	7'	C	.9998	.8767	.1632	7.52
13	C	.6357	.2861	.2968	6.19	8'	O	.9312	.0512	.0490	5.25
14	C	.6824	.4099	.2675	7.02	9'	C	.9141	.0249	.2867	8.36
15	C	.6763	.4424	.1273	6.70	10'	C	.9173	.7779	.7712	7.08
16	C	.6007	.4065	.0590	5.86	1"	C	.8470	.5972	.4524	13.29
17	C	.5461	.2731	.7375	4.51	2"	C	.8162	.5061	.5478	11.30
18	C	.5167	.1300	.7284	6.66	3"	C	.8340	.3828	.5507	10.31
19	C	.5378	.3506	.6019	8.18	4"	C	.8870	.3225	.5158	10.76
20	C	.8001	.3946	.1064	5.40	5"	C	.9281	.3923	.4417	12.59
21	C	.7719	.1385	.9358	4.19	6"	C	.9153	.5294	.4060	11.38
22	C	.7711	.9926	.8879	3.95						

(3) was carried out. The structure thus obtained was refined by successive three-dimensional Fourier syntheses and the least-squares methods. The R factor for 2480 data ($\sin^2\theta/\lambda^2 < 0.35$) is 19.30 % at

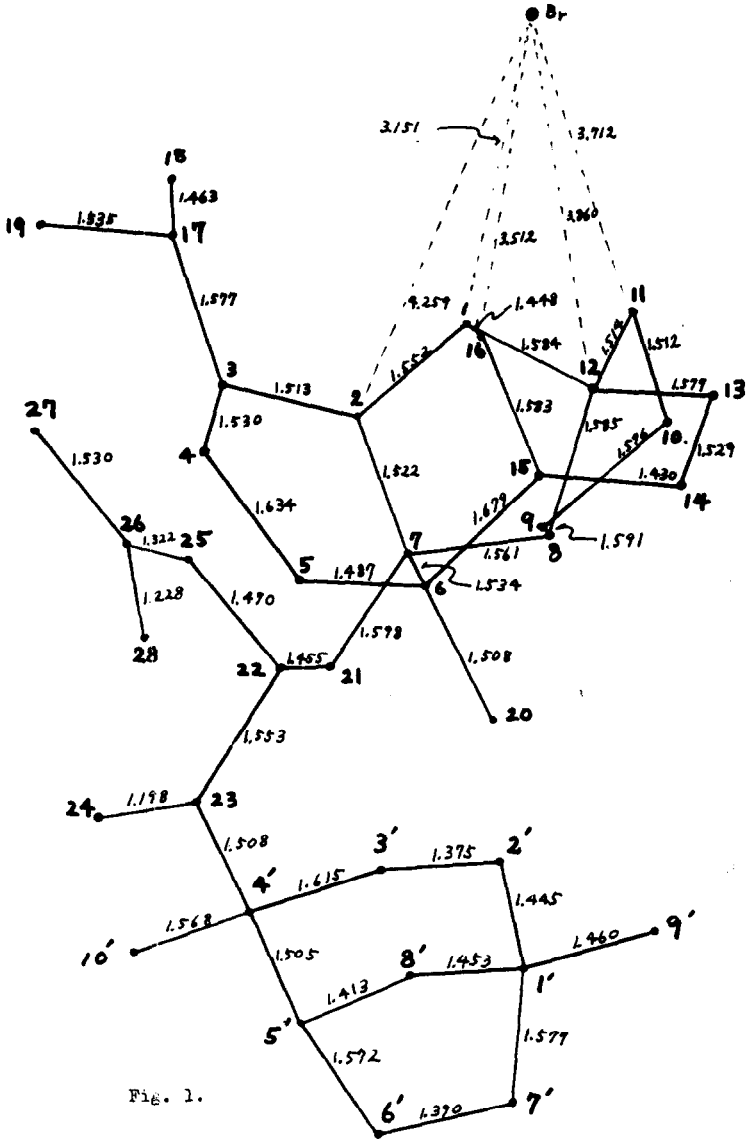
Br
3.151
3.712
3.960
3.512
18
1.463
19
1.835
17
1.577
9.259
1
1.448
11
3
1.513
2
1.552
16
1.584
12
1.512
1.579
13
27
1.530
4
1.530
1.583
1.585
10
1.529
1.522
15
1.430
14
1.634
1.679
9
1.591
26
1.322
25
1.561
8
5
1.487
7
1.534
6
1.228
1.490
28
1.578
1.508
22
1.455
21
20
1.553
24
1.198
23
1.508
3'
1.375
2'
4'
1.615
1.445
1.568
9'
10'
1.505
8'
1.453
1.460
1'
1.413
5'
1.577
1.592
6'
1.370
7'

Fig. 1.

the present stage. The atomic co-ordinates and the temperature factors are listed in Table 1. The atoms numbered 1" to 6", which belong to benzene, gave relatively high temperature factors. This may be due to the fact that the benzene molecules were lost rapidly in atmosphere to give opaque crystals.

Fig. 2.

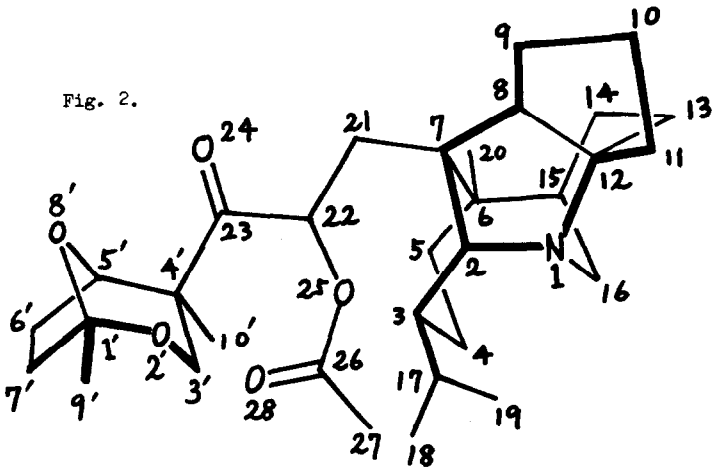

Fig. 1 shows the molecular framework projected along the b axis and bond lengths, and the bond angles are reasonable. The complete chemical formula of daphniphylline hydrobromide is illustrated in Fig. 2. The calculations were performed on the NEAC-2206 electronic computer using our programs.

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