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Structure of a New Daphniphyllum Alkaloid, Daphnilactone B, by Direct Phase Determination

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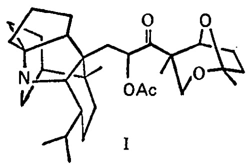
The structures of alkaloids isolated from *Daphniphyllum macropodum* Miquael have been classified into four complex ring systems. The new alkaloid, daphnilactone B, which was isolated from the fruit of the same plant, belongs to a new class. The compound crystallizes with four benzene molecules in the tetragonal space group $P4_12_12$ (or the enantiomorphous $P4_32_12$): $a = 8{\cdot}580 \pm 0{\cdot}0001$, $c = 55{\cdot}529 \pm 0{\cdot}005$ Å. The intensities were obtained from a crystal enclosed in a glass capillary on a four-circle diffractometer. Phases were determined directly from the structure-factor magnitudes by the symbolic addition procedure. The final R index for anisotropic refinement was 5·7% for 1902 observed reflexions. The structure of this alkaloid is characterized by a seven-membered lactone fused with a seven-membered and two six-membered rings.

Introduction

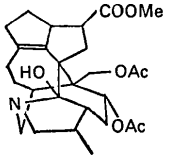
The presence of alkaloids in *Daphniphyllum macropodum* Miquael (Japanese name: Yuzuriha) was first reported by Yagi (1909). The first isolation and structure determination of the alkaloids were carried out by Sakabe, Irikawa, Sakurai & Hirata (1966). Until then, sixteen alkaloids had been isolated from the bark and leaves of the same plant and these were summarized in a paper by Toda, Irikawa, Yamamura & Hirata (1970). These daphniphyllum alkaloids have new complex carbon skeletons. Generally from a structural point of view, the daphniphyllum alkaloids have been classified into four groups [the daphniphylline (I) (Sakabe, Irikawa, Sakurai & Hirata, 1966), yuzurimine (II) (Sakurai, Sakabe & Hirata, 1966), secodaphniphylline (III) (Sasaki & Hirata, 1971), and daphnilactone A (IV) (Sasaki & Hirata, 1972*a*) groups]. This new alkaloid, daphnilactone B* ($C_{22}H_{31}O_2N$), is a major component of the alkaloids in the fruit, but it has never been obtained from the other parts of this plant.

Daphnilactone B is considered to be a new type of alkaloid from a comparison of its spectral and chemical properties with those of other alkaloids. The spectral data of daphnilactone B indicate that the alkaloid has a secondary methyl group [^{1}Hδ($CDCl_3$) 1·00 ppm, 3H, $d, J = 6$Hz], a vinyl proton (δ5·67, 1H), and a lactone ring (ν_{max} (KBr) 1726 cm^{-1}) (Sasaki & Hirata, 1972*b*).

From a biogenetic point of view, we considered that daphniphyllum alkaloids had a plausible common precursor (V), from which the four different kinds of alkaloids were derived as a result of bond formation. A structure determination of daphnilactone B was undertaken to clarify the biogenesis of daphniphyllum alkaloids.



I



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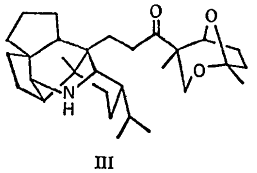

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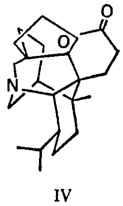

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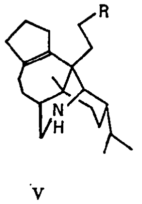
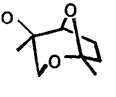


V

R=COOMe

or R=CO



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* The isolation and chemical properties of this compound will be reported in detail elsewhere.

Crystal data

Daphnilactone B benzene solvate, $C_{22}H_{31}O_2N.\frac{1}{2}C_6H_6$, M.W. 380·53, m.p. 92–94°. Tetragonal, $a=8{\cdot}580\pm0{\cdot}001$, $c=55{\cdot}529\pm0{\cdot}005$ Å. $V=4087{\cdot}85$ Å^3 [Cu $K\alpha$ ($\lambda=1{\cdot}54182$ Å) radiation was used]. $D_m=1{\cdot}244$ g cm^{-3} (by flotation in a mixture of n-hexane and carbon tetrachloride), $D_c=1{\cdot}236$ g cm^{-3}, $Z=8$. $F(000)=1656$. Systematic absences: $h00$ absent when h is odd. $00l$ absent when $l\neq4n$. Space group $P4_12_12$ (or the enantiomorphous $P4_32_12$). Linear absorption coefficient μ(Cu $K\alpha$) $=7{\cdot}13$ cm^{-1}.

Experimental

Daphnilactone B was crystallized from a mixture of benzene and n-hexane as colourless plates. The three-dimensional intensity data were collected on a Hilger and Watts automatic four-circle diffractometer Y-290 controlled by a PDP-8 computer. Integrated intensities were measured for $\theta\leq70°$ by the θ–2θ step-scan technique using Cu $K\alpha$ radiation and a scintillation counter. Reflexions ($\theta>50°$) were integrated in 40 steps with intervals of 0·02° and reflexions ($\theta>50°$) were integrated in 50 steps with the same intervals. In this way 2237 independent reflexions were recorded, of which 1903 had intensities more than $3\sigma(F)$ (Sasaki & Hirata, 1971). The analysis was carried out using the 1903 reflexions. The intensities were corrected for Lorentz and polarization factors, and the structure amplitudes were derived. No absorption and extinction corrections were applied since the specimen was considered to be sufficiently small (0·25 × 0·25 × 0·15 mm). Normalized structure factors $|E|$ were then computed. The relationship between $|E|$ and $|F|$ for space group $P4_12_12$ is

$$|E_{\mathbf{h}}|^2=|F_{\mathbf{h}}|^2/\varepsilon\sum_{j=1}^{N}f_{j\mathbf{h}}$$

where the $|F_{\mathbf{h}}|^2$ values are those from which the effects of thermal motion have been removed, $\varepsilon=1$ except for $00l$ where $\varepsilon=4$, for $hk0(h=\pm k)$, $h00$ and $0k0$ where $\varepsilon=2$, N is the number of atoms in the unit cell, and $f_{j\mathbf{h}}$ is the atomic scattering factor for the jth atom. The statistical averages $\langle|E|\rangle$ and $\langle|E^2-1|\rangle$ were 0·88 and 0·79 respectively. They may be compared with 0·89 and 0·74 calculated for a noncentrosymmetric crystal with atoms in random positions.

Determination and refinement of the structure

The structure of daphnilactone B was solved by the $\sum_2$ relationship and the tangent formula (Karle & Karle, 1966). It is possible to isolate an origin in space group $P4_12_12$ by fixing the phases of two reflexions, which have two possible values differing by π (Hauptman & Karle, 1956). We could find only two two-dimensional reflexions of suitable parity among the larger $|E|$ values, 0,1,69 and 0,5,28, and assigned to them the phases of $\pi/4$ and $\pi/2$, respectively. Further the phases of three reflexions were selected as a starting set, and two of these were restricted to two values differing by π. These initial assignments are listed in Table 1.

Table 1. *Phase assignments for implementing equation* (1)

$\|E\|$	h	k	l	φ	
2·66	0	1	69	$\pi/4$	Origin assignment
3·43	0	5	28	$\pi/2$	
2·48	0	5	33	a ($\pi/4$ or $-3\pi/4$)	
3·20	2	2	13	b ($\pi/2$ or $-\pi/2$)	
3·08	2	3	49	c	

Next we used the formula (1) for 187 reflexions ($|E|>1{\cdot}6$) in order to assign a phase to reflexion 2,3,49;

$$\varphi_{\mathbf{h}}\simeq\langle\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}\rangle_{\mathbf{k}}\,. \tag{1}$$

From multiple indications we assigned $c=\pi/2$ or $-\pi/2$. Further we applied the tangent formula

$$\tan\varphi_{\mathbf{h}}\simeq A/B\,, \tag{2}$$

where

$$A=\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\,,$$

$$B=\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}).$$

The tangent formula was only applied to the 187 reflexions with $|E|$ values greater than 1·6. The consistency of a phase determined from the tangent formula can be judged from the value of the parameter $t_{\mathbf{h}}$, where

$$t_{\mathbf{h}}=(A^2+B^2)^{1/2}/\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\,. \tag{3}$$

We required this parameter $t_{\mathbf{h}}$ to be greater than the arbitrary value of 0·4 and the variance to be less than 0·5. If these criteria were satisfied, a phase determined by the tangent formula was subsequently used in the next cycle. After 6 cycles an index C was compared for each set. This index C (Germain & Woolfson, 1968, is defined as:

$$Z_{\mathbf{h}}=A^2+B^2\,, \tag{4}$$

$$C=\sum_{\mathbf{h}}Z_{\mathbf{h}}\,. \tag{5}$$

Table 2 shows the C value, the Q value (Drew, Templeton & Zalkin, 1969), and a number of accepted phases for each starting set. Subsequently, the tangent formula was computed using 467 reflexions ($|E|>1{\cdot}2$), based on 148 phases in the most consistent set ($C=137\times10^4$), and 312 phases of the 467 were acceptable. An E map was calculated with these and the 25 strongest peaks appeared to correspond with all non-hydrogen atoms of daphnilactone B except those in the solvated benzene. The initial R value, based on the coordinates of the atoms as obtained from the E map and an overall isotropic thermal factor of 3·90 Å^2, was 30·7 %. Refinement proceeded to an R value of 21·5 % with individual isotropic thermal motion. At this stage, a difference Fourier map was computed, and the solvated benzene molecule appeared on a twofold axis. Further refinement led to an R value of 14·7 % with individual isotropic thermal motion and of 9·5 % with 3 cycles of anisotropic refinement. At this stage, 31 hydrogen atoms of the alkaloid molecule were clearly visible in a difference map. The hydrogen atoms were given constant anisotropic thermal factors equal to those of the carbon atom which they were attached, and no attempt was made to determine their individual motions. Their positions were refined, however, with the thermal factors of their heavier bonding atoms, leading to an R value of 5·7 %. Possible positions for the four solvated-benzene hydrogen atoms on C(26–29) were indicated weakly in a subsequent difference map. Attempts to refine these positions by least-squares refinement led to large oscillating shifts. Coordinates obtained from the difference map are listed for these four atoms with least-squares results for all other atoms in Table 3 and 4. The final R value computed with the reported parameters was 5·7 % omitting unobserved reflexions. Unit weight was given to all the reflexions.

Table 2. *Comparison of eight starting sets*

	1	2	3	4	5	6	7	8
$a=$	$\pi/4$	$\pi/4$	$\pi/4$	$\pi/4$	$-\pi/4$	$-\pi/4$	$-\pi/4$	$-\pi/4$
$b=$	$\pi/2$	$-\pi/2$	$\pi/2$	$-\pi/2$	$\pi/2$	$-\pi/2$	$\pi/2$	$-\pi/2$
$c=$	$\pi/2$	$\pi/2$	$-\pi/2$	$-\pi/2$	$\pi/2$	$\pi/2$	$-\pi/2$	$-\pi/2$
C*	72	113	137	91	126	64	73	117
R(%)	29	33	32	27	33	29	31	31
N†	116	133	148	131	127	97	111	138

* The C values are multiplied by 10^4.
† Number of accepted phases.

The strong reflexion, 004, was assumed to be affected by extinction and therefore excluded from the refinement. After the last cycle of refinement, the average shift in parameters was 0·1σ and no shift was greater than 0·4σ.

Coordinates, thermal parameters, and the scale factor were refined by the block-diagonal approximation of the least-squares method, in which the expression $\sum w(|F_o|-|F_c|)^2$ is minimized. The matrices used were 9 × 9 for coordinates and thermal parameters (4 × 4 for isotropic thermal motion) of each atom. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Observed and calculated structure factors are listed in Table 5.

Table 3. *Fractional atomic coordinates and thermal parameters for daphnilactone B benzene solvate*

Thermal parameters are of the form $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh)]$. The β_{ij}'s are multiplied by 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
N(1)	0·8777	0·2243	0·1532	139	101	2	−29	2	−5
C(2)	0·9695	0·1198	0·1688	123	91	2	−17	−4	3
C(3)	0·8527	0·0011	0·1788	129	89	3	−26	3	−2
C(4)	0·7521	0·0709	0·1990	133	145	2	−43	1	4
C(5)	0·8475	0·1741	0·2159	137	133	2	−7	−1	6
C(6)	0·9597	0·2960	0·2036	116	76	2	25	0	−2
C(7)	1·0730	0·2100	0·1866	107	78	2	−9	1	3
C(8)	1·1853	0·3129	0·1716	122	97	2	−11	3	−5
C(9)	1·2697	0·2569	0·1534	152	132	3	−8	0	6
C(10)	1·3557	0·3782	0·1397	151	175	4	−39		16
C(11)	1·3509	0·5176	0·1566	213	189	4	−132	5	6
C(12)	1·2071	0·4886	0·1734	207	111	3	−53	2	7
C(13)	1·0628	0·5788	0·1653	235	87	4	17	7	5
C(14)	0·9306	0·5741	0·1838	209	85	3	47	1	−2
C(15)	0·8591	0·4128	0·1892	152	98	2	51	−2	−5
C(16)	0·7862	0·3440	0·1659	193	105	3	47	3	−10
C(17)	0·7619	−0·0368	0·1553	137	95	3	−56	−4	−5
C(18)	0·7761	0·1154	0·1402	209	124	3	−33	−7	−17
C(19)	0·5946	−0·0955	0·1582	166	190	4	−118	−5	−7
C(20)	1·0383	0·3853	0·2243	156	106	2	13	−2	−3
C(21)	1·1770	0·0914	0·2004	124	104	3	36	3	−1
C(22)	1·2846	0·1656	0·2193	127	154	3	47	2	−7
C(23)	1·2040	0·1883	0·2430	170	170	3	−24	4	−16
O(24)	1·0847	0·2883	0·2446	157	154	2	−2	1	−4
O(25)	1·2387	0·1176	0·2608	277	266	3	147	17	−17
C(26)	−0·0037	−0·0037	0·0	297	297	12	−386	60	−60
C(27)	0·0041	0·0998	0·0183	241	423	8	−20	41	−13
C(28)	0·1166	0·2127	0·0184	259	238	12	80	−13	−31
C(29)	0·2176	0·2176	0·0	199	199	15	67	12	−12
Standard deviations									
N(1)	0·0004	0·0004	0·0001	6	5	0	10	1	1
O(23, 24)	0·0005	0·0005	0·0001	7	7	1	12	1	1
C(2–23)	0·0005	0·0005	0·0001	7	7	0	12	1	1
C(26–29)	0·0010	0·0010	0·0001	20	21	1	32	7	7

Table 4. *Fractional atomic coordinates for the hydrogen atoms*

	x	y	z
H(2)	1·0469	0·0611	0·1575
H(3)	0·9113	−0·0980	0·1874
H(4*a*)	0·6992	−0·0160	0·2093
H(4*b*)	0·6630	0·1374	0·1923
H(5*a*)	0·9109	0·0970	0·2269
H(5*b*)	0·7664	0·2269	0·2272
H(9)	1·2688	0·1451	0·1494
H(10*a*)	1·4656	0·3449	0·1360
H(10*b*)	1·2950	0·4054	0·1235
H(11*a*)	1·4536	0·5156	0·1679
H(11*b*)	1·3374	0·6209	0·1467
H(12)	1·2268	0·5267	0·1916
H(13*a*)	1·0938	0·6888	0·1637
H(13*b*)	1·0200	0·5272	0·1489
H(14*a*)	0·9735	0·6190	0·2002
H(14*b*)	0·8342	0·6495	0·1782
H(15)	0·7684	0·4411	0·2016
H(16*a*)	0·7709	0·4295	0·1533
H(16*b*)	0·6798	0·2878	0·1723
H(17)	0·8233	−0·1314	0·1460
H(18*a*)	0·8338	0·0882	0·1236
H(18*b*)	0·6654	0·1674	0·1378
H(19*a*)	0·5352	0·0049	0·1677
H(19*b*)	0·5576	−0·1238	0·1408
H(19*c*)	0·5914	−0·1795	0·1683
H(20*a*)	1·1319	−0·4336	0·2190
H(20*b*)	0·9562	0·4655	0·2320
H(21*a*)	1·2416	0·0482	0·1890
H(21*b*)	1·1072	0·0112	0·2093
H(22*a*)	1·3778	0·0855	0·2234
H(22*b*)	1·3153	0·2706	0·2138
H(26)*	−0·085	−0·085	0·0
H(27)*	−0·064	0·101	0·030
H(28)*	0·114	0·292	0·032
H(29)*	0·305	0·305	0·0
Standard deviations:			
	0·0060	0·0060	0·0007

* Indicated atoms were not refined by least-squares; their positions were estimated (±0·007) from a difference map.

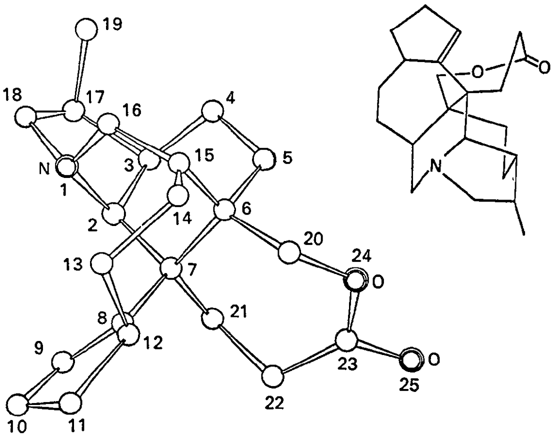

Fig. 1. The configuration of daphnilactone B

Table 5. *Observed and calculated structure factors*

The columns represent the index l, $|F_o|$, $|F_c|$ and φ_{calc} (°).

Discussion

The molecular structure and conformation is illustrated Fig. 1. The structure is in agreement with the results from n.m.r. and mass spectra measurements. The ring system of daphnilactone B does not appear to fit any naturally occurring system. The molecule is characterized by the C(8)–C(9) double bond and the seven-membered lactone ring fused with three rings (cycloheptane, cyclohexane, and piperidine). This alkaloid belongs to a new group of daphniphyllum alkaloids, which can be derived from the common precursor (V) as a result of the N(1)–C(18) bond formation and the double bond migration.

The bond lengths and angles for non-hydrogen atoms are shown in Table 6 and Fig. 2. The range of e.s.d.'s for the bond lengths of the daphnilactone B, and of the solvated benzene molecule with the larger thermal vibration are 0·005∼0·007 and 0·012∼0·017 Å respectively. The range of e.s.d.'s for the valency angle of daphnilactone B and the solvated benzene molecule

Table 5 (*cont.*)

are 0·3∼0·5 and 0·9∼1·2° respectively. These e.s.d.'s were derived from the least-squares block-diagonal approximation. The average values of bond distances for various types of bond have been calculated as 1·540 for C–C, 1·472 for C–N, 1·339 for aromatic C–O, 1·336 for C=C, 1·196 for a lactone C=O, and 1·353 Å for the solvated-benzene aromatic bonds, and these values are in agreement with the expected ones. The bond lengths of daphnilactone B are shown Fig. 2.

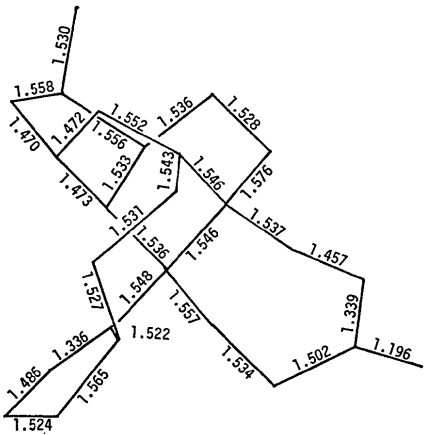

Fig. 2. Bond lengths in daphnilactone B

Table 6. *Bond lengths and angles in daphnilactone B benzene solvate*

	Distance (Å)	Angle	θ(°)
N(1)—C(2)	1·473	C(2)—N(1)—C(16)	115·5
N(1)—C(16)	1·472	C(2)—N(1)—C(18)	102·7
N(1)—C(18)	1·470	C(16)-N(1)—C(18)	111·3
C(2)—C(3)	1·533	N(1)—C(2)—C(3)	105·5
C(2)—C(7)	1·536	N(1)—C(2)—C(7)	112·3
		C(3)—C(2)—C(7)	118·6
C(3)—C(4)	1·536	C(2)—C(3)—C(4)	111·9
C(3)—C(17)	1·556	C(2)—C(3)—C(17)	99·3
		C(4)—C(3)—C(17)	114·4
C(4)—C(5)	1·528	C(3)—C(4)—C(5)	111·9
C(5)—C(6)	1·576	C(4)—C(5)—C(6)	116·6
C(6)—C(7)	1·546	C(5)—C(6)—C(7)	109·4
C(6)—C(15)	1·546	C(5)—C(6)—C(15)	108·3
C(6)—C(20)	1·537	C(5)—C(6)—C(20)	106·1
		C(7)—C(6)—C(15)	110·0
		C(7)—C(6)—C(20)	114·9
		C(15)-C(6)—C(20)	108·1
C(7)—C(8)	1·548	C(2)—C(7)—C(6)	105·7
C(7)—C(21)	1·557	C(2)—C(7)—C(8)	107·6
		C(2)—C(7)—C(21)	108·6
		C(6)—C(7)—C(8)	116·6
		C(6)—C(7)—C(21)	111·7
		C(8)—C(7)—C(21)	106·3
C(8)—C(9)	1·336	C(7)—C(8)—C(9)	122·6
C(8)—C(12)	1·522	C(7)—C(8)—C(12)	127·4
		C(9)—C(8)—C(12)	109·8
C(9)—C(10)	1·486	C(8)—C(9)—C(10)	114·0
C(10)-C(11)	1·524	C(9)—C(10)—C(11)	102·7
C(11)-C(12)	1·565	C(10)-C(11)-C(12)	105·3
C(12)-C(13)	1·527	C(8)—C(12)-C(11)	102·5
		C(8)—C(12)-C(13)	112·5
		C(11)-C(12)-C(13)	112·5
C(13)-C(14)	1·531	C(12)-C(13)-C(14)	112·9
C(14)-C(15)	1·543	C(13)-C(14)-C(15)	116·7
C(15)-C(16)	1·552	C(6)—C(15)-C(14)	117·4
		C(6)-C(15)—C(16)	114·2
		C(14)-C(15)-C(16)	109·8
		N(1)—C(16)-C(15)	116·6
C(17)-C(18)	1·558	C(3)—C(17)-C(18)	103·8
C(17)-C(19)	1·530	C(3)—C(17)-C(19)	116·8
		C(18)-C(17)-C(19)	113·9
		N(1)—C(18)-C(17)	108·2
C(20)-O(24)	1·457	C(6)—C(20)-O(24)	114·4
C(21)-C(22)	1·534	C(7)—C(21)-C(22)	114·3
C(22)-C(23)	1·502	C(21)-C(22)-C(23)	112·1
C(23)-O(24)	1·339	C(22)-C(23)-O(24)	119·6
C(23)-O(25)	1·196	C(2)-C(23)-O(25)	123·0
		O(24)-C(23)-O(25)	117·4
		C(20)-O(24)-C(23)	121·6
C(26)-C(27)	1·350	C(26)-C(27)-C(28)	120·4
C(27)-C(28)	1·368	C(27)-C(28)-C(29)	118·2
C(28)-C(29)	1·342		
		C(27)-C(26)-C(27′)*	120·0
		C(28)-C(29)-C(28′)*	122·8

* A solvated benzene ring consists of C(26–29) and C(27′–28′), of which C(27′) and C(28′) correspond to C(27) and C(28) through a symmetry operation.

The structure is hexacyclic and four rings (seven-membered lactone, cycloheptane, cyclohexane, and piperidine) have the C(7) and the C(8) atom in common giving a complex bicyclo system. The 2-azabicyclo-

[3,3,1]nonane ring system, fused with the cyclopentane, the cycloheptane and the seven-membered lactone ring, consists of two slightly distorted six-membered rings. The 2-azabicyclo[3,3,1]nonane ring atoms N(1), C(2) C(6), C(15) and C(2), C(3), C(5), C(6) are coplanar to within 0·009 and 0·024 Å respectively. The dihedral angle between the two planes is 72·8°, and the non-bonded distance in the ring system between C(4) and C(16) is 2·99 Å, which is in agreement with the values of other daphniphyllum alkaloids. The cyclopentane ring is a deformed β envelope and the ring atoms N(1), C(3), C(17), and C(18) are coplanar to within 0·027 Å (Table 7). The cyclopentane ring plane makes a dihedral angle of 49-50° with the two planes through each four caplanar atoms of the 2-azabicyclo[3,3,1]nonane ring. The cyclopentane ring is fused with the cycloheptane ring, and the cyclopentene ring atoms [C(8), C(9), C(10), and C(12) are coplanar to within 0·009 Å. The ring system of daphnilactone B is rigid, but only the conformation of the seven-membered lactone ring is not determined by fusion with other rings. The seven-membered lactone ring adopts a twisted *trans* conformation with the lactone group, C(22), C(23), O(24), and O(25), coplanar and C(20) above this plane by 0·077 Å. This ring is *trans* fused to the piperidine ring, but it is *cis* fused to the cyclohexane and the cycloheptane ring bearing the cyclopentene ring. Therefore, the seven-membered lactone ring atoms have a non-bonded interaction with the cyclohexane and cyclopentene rings (Table 8). The non-bonded distances O(24)···C(5) and C(22)···C(8) are 2·77 and 3·05 Å respectively.

There are several bicyclic systems fused to each other and this imposes considerable strains on the molecule.

Table 7. *Least-squares planes*

Plane 1 (Lactone group)	Δ	Plane 2 (Cyclopentene ring)	Δ	Plane 3 (Cyclohexane ring)	Δ
C(22)	−0·003 Å	C(8)	−0·009 Å	C(2)	0·024 Å
C(23)	0·010	C(9)	0·009	C(3)	−0·023
O(24)	−0·003	C(10)	−0·005	C(5)	0·023
O(25)	−0·004	C(12)	0·005	C(6)	−0·023
C(20)*	0·077	C(7)*	−0·151	C(4)*	−0·543
		C(11)*	0·380	C(7)*	0·717

Plane 4 (Piperidine ring)		Plane 5 (Solvated benzene)		Plane 6 (Cyclopentane ring)	
N(1)	0·008	C(26)	0·000	N(1)	0·017
C(2)	−0·009	C(27)	0·002	C(3)	−0·016
C(6)	0·008	C(28)	−0·002	C(17)	0·025
C(15)	−0·008	C(29)	0·000	C(18)	−0·027
C(7)*	0·778	C(27′)	−0·002	C(2)*	0·645
C(16)*	−0·398	C(28′)	0·002		

* Atoms excluded from the calculation of the plane.

Equations of the planes are of the type $hx+ky+lz=m$
x,y,z, are coordinates in Å.

	h(Å)	k(Å)	l(Å)	m(Å)
1:	0·6428	0·7276	0·2395	11·0379
2:	0·7859	−0·1283	0·6049	13·4210
3:	0·7721	−0·4962	0·3971	9·6099
4:	0·8350	0·4546	−0·3099	4·5175
5:	−0·6140	0·6140	−0·4960	0·0000
6:	0·8187	−0·3880	−0·4233	1·7991

Some dihedral angles between planes.

∠1,2	∠2,3	∠2,4	∠3,4	∠3,6	∠4,6
56·2°	24·4°	65·8°	72·8°	49·0°	50·3°

Table 8. *Some intramolecular non-bonded contacts*

C(4)....C(16)	2·99Å	C(21)...C(3)	3·13Å
C(20)....C(5)	2·49	C(22)...C(8)	3·05
C(20)...C(15)	2·49	C(22)...C(6)	3·13
C(20)....C(8)	3·25	C(23)...C(6)	3·17
C(21)....C(2)	2·52	C(23)...C(5)	3·41
C(21)....C(6)	2·58	O(24)...C(6)	2·51
C(21)....C(5)	3·05	O(24)...C(5)	2·75
C(21)....C(9)	3·09		

Table 9. *Torsional angles*

For definition see Klyne & Prelog (1960)

2-Azabicyclo[3,3,1]nonane ring

C(16)-N(1)—C(2)—C(7)	+52·1°
N(1)—C(2)—C(7)—C(6)	−65·4
C(2)—C(7)—C(6)—C(15)	+62·2
C(7)—C(6)—C(15)-C(16)	−47·5
C(6)—C(15)-C(16)-N(1)	+32·8
C(15)-C(16)-N(1)—C(2)	−34·6
C(7)—C(2)—C(3)—C(4)	−50·4
C(2)—C(3)—C(4)—C(5)	+40·9
C(3)—C(4)—C(5)—C(6)	−47·1
C(4)—C(5)—C(6)—C(7)	+56·6
C(5)—C(6)—C(7)—C(2)	−56·6
C(6)—C(7)—C(2)—C(3)	+58·1
C(16)-N(1)—C(2)—C(3)	−78·5
N(1)—C(2)—C(3)—C(4)	+76·4
C(4)—C(5)—C(6)—C(15)	−63·2
C(5)—C(6)—C(15)-C(16)	+72·0

Cyclopentane ring (1, 2, 3, 17, 18)

C(18)-N(1)—C(2)—C(3)	+42·9
N(1)—C(2)—C(3)—C(17)	−44·7
C(2)—C(3)—C(17)-C(18)	+28·5
C(3)—C(17)-C(18)-N(1)	−4·5
C(17)-C(18)-N(1)—C(2)	−22·9

Cycloheptane ring (6, 7, 8, 12, 13, 14, 15)

C(15)—C(6)-C(7)—C(8)	−56·4
C(6)—C(7)—C(8)—C(12)	−5·8
C(7)—C(8)—C(12)-C(13)	+66·7
C(8)—C(12)-C(13)-C(14)	−74·3
C(12)-C(13)-C(14)-C(15)	+63·7
C(13)-C(14)-C(15)-C(6)	−71·3
C(14)-C(15)-C(6)—C(7)	+83·2

Cyclopentene ring (8, 9, 10, 11, 12)

C(12)-C(8)—C(9)—C(10)	+1·7
C(8)—C(9)—C(10)-C(11)	−16·2
C(9)—C(10)-C(11)-C(12)	+23·1
C(10)-C(11)-C(12)-C(8)	−22·3
C(11)-C(12)-C(8)—C(9)	+13·1

Lactone ring (6, 7, 21, 22, 23, 24, 20)

C(20)-C(6)—C(7)—C(21)	−57·7
C(6)—C(7)—C(21)-C(22)	+62·6
C(7)—C(21)-C(22)-C(23)	−85·3
C(21)-C(22)-C(23)-C(24)	+65·5
C(22) C(23) C(24)-C(20)	+4·9
C(24) C(24)-C(20)-C(6)	−71·2
C(24)-C(20)-C(6)—C(7)	+80·0

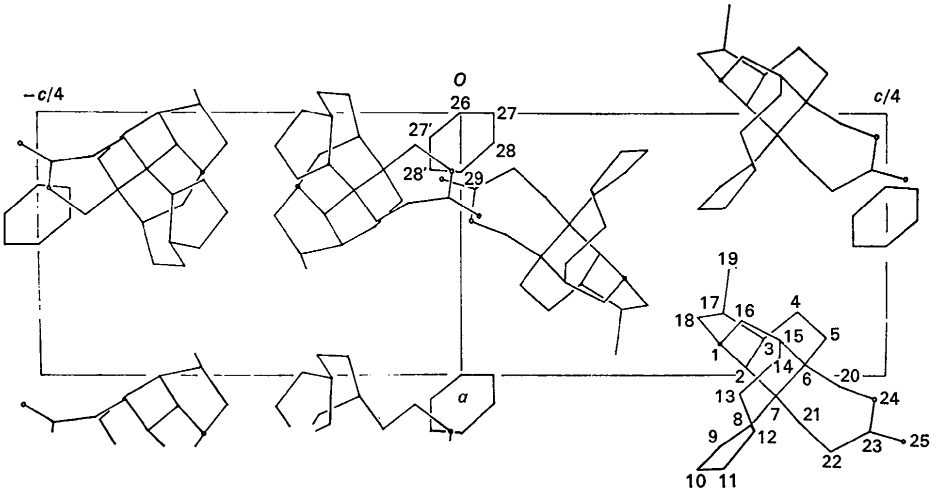

Fig. 3. The arrangement of the molecules of daphnilactone B in half the unit cell, as viewed along the *b* axis.

Many of the rings are therefore distorted from ideal conformations (Bucourt & Hainaut, 1965). This can be seen also from the torsional angles (Table 9).

The molecular packing arrangement along the *b* axis is illustrated in Fig. 3. The intermolecular contacts between a daphnilactone B and a solvated benzene molecular are greater than 3·48 Å. The shortest intermolecular distances 3·33 Å for C···O and 3·73 Å for C···C. All intermolecular contacts were calculated, and the most significant contacts are given in Table 10.

Table 10. *Shorter intermolecular contacts* (< 3·8 Å)

		Symmetry operation on primed atoms
C(26)···C(23′)	3·71 Å	$y-0{\cdot}5,\ -x+1{\cdot}5,\ z-0{\cdot}25$
C(27)···C(23′)	3·48	
C(27)···C(24′)	3·53	
C(28)···C(24′)	3·57	
C(29)···O(25′)	3·50	$-x+1{\cdot}5,\ y+0{\cdot}5,\ -z-0{\cdot}75$
C(25)···C(27′)	3·62	$-y+1{\cdot}5,\ x+0{\cdot}5,\ z+0{\cdot}25$
C(4)····C(24′)	3·42	
O(24)···C(5′)	3·33	
C(4)····O(25′)	3·65	
C(5)····O(25′)	3·78	$-y+1{\cdot}0,\ -x+1{\cdot}0,\ -z+1{\cdot}5$
C(14)···O(25′)	3·50	$-y+1{\cdot}0,\ -x+2{\cdot}0,\ -z+0{\cdot}5$
C(20)···O(25′)	3·59	
C(3)····C(14′)	3·73	$x\quad y-1{\cdot}0,\ z$
C(19)···N(1′)	3·75	$-x+1{\cdot}5,\ y-0{\cdot}5,\ -z+0{\cdot}5$

All computations were performed on a FACOM 230-60 at Nagoya University Computation Centre using our programs.

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