This geometry can be explained by two particular interactions: that between C(9) and O(2) and that between the vinyl H and O(1). The former is one of repulsion, as indicated by a distance of 2·90 Å which, however, is shorter than the sum of the respective van der Waals radii. The second interaction is one of attraction and the relative positions of H, O(1) and C(7) [C···O = 2·69, H···O = 2·02 Å; ∠C–H···O = 121·2°] may suggest the formation of a C–H···O hydrogen bond.

Finally the phenyl ring makes an angle of 88·5° with the vinyl plane.

As for the crystal packing, all the intermolecular distances correspond to standard van der Waals contacts.

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The Borine Adduct of Condylocarpine: A Case of Partially Mistaken Identity

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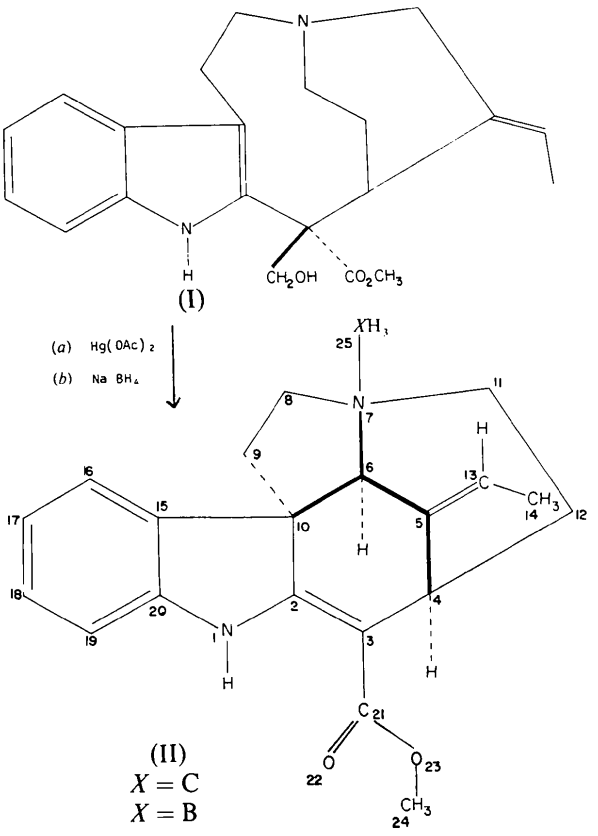
Abstract. $C_{20}H_{25}O_2N_2B$, orthorhombic, a = 10·267 (5), b = 16·553 (11), c = 10·858 (7) Å, Z = 4, $P2_12_12_1$. Final R is 0·061 (1472 reflections). The structure and stereochemistry of the borine adduct of the alkaloid condylocarpine have been determined. The H atoms on B are staggered with respect to the three N–C bonds. Bond lengths and angles are in general agreement with accepted values.

Introduction. Some time ago, we were provided with crystals of a hitherto unknown compound that had been obtained by the action of mercuric acetate on the alkaloid stemmadenine (I) (Scott, 1971). The product was believed to have the molecular formula $C_{21}H_{24}O_2N_2$ (M_r = 336) and had been prepared by a mild route in a biosynthetic investigation. An X-ray analysis was undertaken to determine the structure. Cell data are as given in the *Abstract*. Systematic absences $h00$, when $h = 2n + 1$, $0k0$, when $k = 2n + 1$, and $00l$, when $l = 2n + 1$ determine the space group as $P2_12_12_1$. Data were collected on a Picker FACS-1 diffractometer (Cu $K\alpha$) and 1472 reflections out of a possible 1806 within the 2θ range 0–132° were considered observed at the 2σ level. Straightforward application of the multiple-solution tangent-formula approach (Germain, Main & Woolfson, 1971) provided a skeleton of non-hydrogen atoms corresponding to (II). Fourier and least-squares refinement gave a structure that had one additional H atom compared with that expected for (II), X = C. If X were C, this would be positively charged and would thus require a corresponding negative charge. However, no evidence could be found, either by formulation of the molecule as a zwitterion or by assuming the presence of an anion in the crystal, for such a negatively charged group.

The difficulty of reconciling the apparent structure with the chemistry caused some delay in the refinement until it was realized that one of the steps following oxidation of (I) had involved treatment with borohydride, and that we were, in fact, dealing with a BH_3, not a CH_3, group on the quaternary N. In particular, the observed N–X length (~1·62 Å) was consistent with that for a B–N bond rather than for a C–N bond, and the product was thus shown to be the BH_3 adduct of the previously characterized alkaloid, condylocarpine (Sandoval, Walls, Shoolery, Wilson, Budzikiewicz & Djerassi, 1962; Biemann, Burlingame & Stauffacher, 1962). Full-matrix least-squares refinement of the



positional and anisotropic thermal parameters for the non-hydrogen atoms and the positional and isotropic thermal parameters for the H atoms gave an R of 0·061 and R_2 of 0·049 for the 1472 observed reflections.*

Discussion. The structure and stereochemistry, as shown in Fig. 1, conform to that generally accepted for condylocarpine, although the stereochemistry of the exocyclic double bond is definitely determined. The absolute stereochemistry of condylocarpine has been related to that of strychnine (Klyne & Buckingham, 1974) and is as shown in Fig. 1. The atom numbering does not correspond to a specific biogenetic scheme. The final atomic coordinates are given in Table 1, while Table 2 contains the bond lengths and angles involving the non-hydrogen atoms. These dimensions are in general agreement with accepted values; the B—N length of 1·623 (6) Å is similar to that of 1·661 (7) Å reported for the B—N length in the hexamethylenetetramine–borine adduct (Hanic & Šubrtová, 1969). Despite the longer bond, the H atoms on the boron are staggered with respect to the three N—C bonds. A stereoscopic drawing of the molecular packing is shown

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32726 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

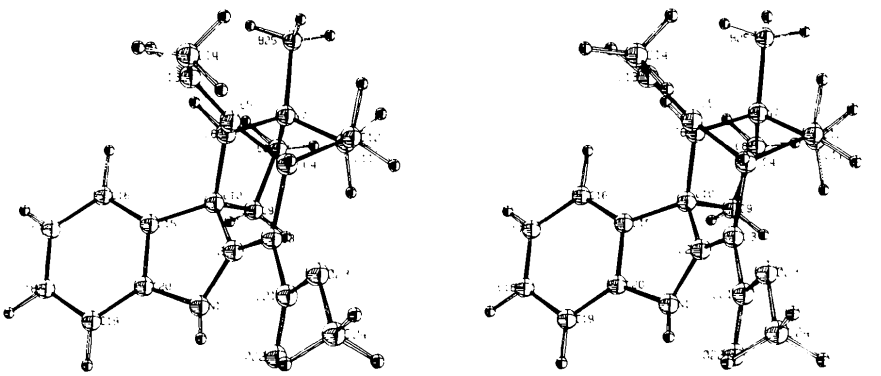


Fig. 1. A stereoscopic view of a single molecule of the borine adduct of condylocarpine.

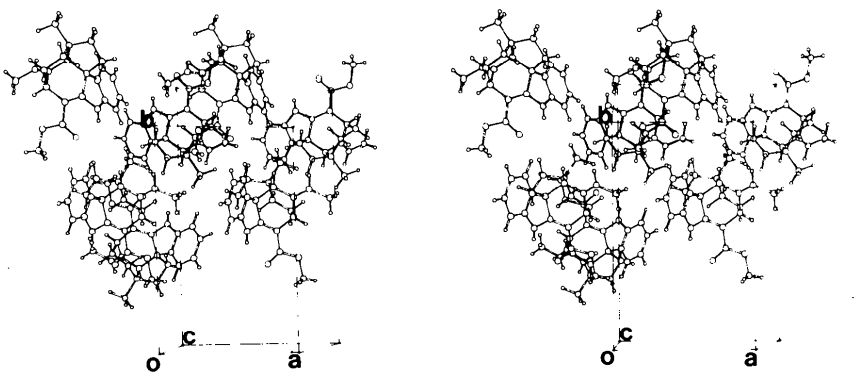


Fig. 2. Stereoscopic view of the molecular packing. The bonds of the reference molecule are darker.

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$)

Estimated standard deviations are given in parentheses.

	x	*y*	*z*
N(1)	−303 (3)	10397 (2)	2006 (3)
C(2)	729 (4)	9991 (3)	2526 (4)
C(3)	1882 (4)	10282 (3)	2927 (4)
C(4)	3035 (4)	9697 (3)	3055 (5)
C(5)	2854 (4)	9001 (3)	2171 (4)
C(6)	1625 (4)	8558 (2)	2464 (4)
N(7)	1634 (4)	8209 (2)	3763 (3)
C(8)	235 (4)	8058 (3)	3998 (5)
C(9)	−486 (4)	8789 (3)	3499 (4)
C(10)	397 (4)	9097 (3)	2401 (4)
C(11)	2076 (5)	8833 (3)	4718 (4)
C(12)	3238 (5)	9329 (3)	4329 (4)
C(13)	3647 (4)	8773 (3)	1279 (5)
C(14)	4902 (6)	9157 (5)	904 (6)
C(15)	−409 (4)	9114 (3)	1235 (4)
C(16)	−792 (5)	8507 (3)	436 (5)
C(17)	−1610 (5)	8732 (3)	−541 (5)
C(18)	−2051 (5)	9503 (3)	−664 (5)
C(19)	−1704 (4)	10113 (3)	156 (5)
C(20)	−871 (4)	9899 (3)	1093 (4)
C(21)	2057 (5)	11157 (3)	2953 (4)
O(22)	1204 (3)	11652 (2)	2853 (4)
O(23)	3328 (3)	11370 (2)	3102 (3)
C(24)	3590 (6)	12233 (3)	3078 (6)
B(25)	2481 (6)	7385 (3)	3881 (6)
H(1)*	−35 (3)	1086 (2)	196 (3)
H(4)	379 (3)	1001 (2)	283 (3)
H(6)	156 (4)	805 (2)	193 (4)
H(8*A*)	0 (4)	749 (3)	349 (4)
H(8*B*)	6 (4)	789 (2)	489 (4)
H(9*A*)	−47 (3)	922 (2)	409 (3)
H(9*B*)	−131 (4)	863 (2)	321 (3)
H(11*A*)	236 (3)	847 (2)	548 (3)
H(11*B*)	121 (4)	922 (2)	499 (4)
H(12*A*)	333 (3)	978 (2)	501 (2)
H(12*B*)	409 (3)	894 (2)	440 (3)
H(13)	350 (3)	829 (2)	65 (3)
H(16)	−42 (4)	792 (2)	57 (3)
H(17)	−187 (3)	832 (2)	−102 (3)
H(18)	−264 (5)	966 (3)	−134 (4)
H(19)	−203 (4)	1065 (2)	6 (4)
H(24*A*)	328 (5)	1244 (2)	387 (4)
H(24*B*)	316 (5)	1244 (3)	231 (4)
H(24*C*)	443 (5)	1231 (3)	316 (4)
H(25*A*)	210 (3)	695 (2)	319 (3)
H(25*B*)	232 (4)	715 (2)	479 (4)
H(25*C*)	354 (4)	764 (2)	370 (4)
H(14*A*)	505 (7)	971 (4)	136 (6)
H(14*B*)	556 (8)	892 (5)	145 (8)
H(14*C*)	502 (8)	917 (4)	2 (7)

* Hydrogen atoms are given the numbers of the atoms to which they are attached.

Table 2. *Bond lengths* (Å) *and angles* (°) *involving the non-hydrogen atoms*

The C–H lengths range from 0·88 (5) to 1·13 (4) Å, the N–H length is 0·77 (3) Å and the B–H lengths range from 1·07 (4) to 1·18 (4) Å. Standard deviations are in parentheses.

N(1)–C(2)	1·376 (5)	C(8)–C(9)	1·518 (7)
N(1)–C(20)	1·415 (6)	C(9)–C(10)	1·582 (6)
C(2)–C(3)	1·350 (6)	C(10)–C(15)	1·513 (6)
C(2)–C(10)	1·525 (7)	C(11)–C(12)	1·509 (7)
C(3)–C(4)	1·536 (6)	C(13)–C(14)	1·493 (8)
C(3)–C(21)	1·460 (7)	C(15)–C(16)	1·385 (7)
C(4)–C(5)	1·511 (7)	C(15)–C(20)	1·392 (7)
C(4)–C(12)	1·526 (7)	C(16)–C(17)	1·403 (7)
C(5)–C(6)	1·494 (6)	C(17)–C(18)	1·361 (7)
C(5)–C(13)	1·320 (7)	C(18)–C(19)	1·393 (7)
C(6)–N(7)	1·524 (5)	C(19)–C(20)	1·376 (7)
C(6)–C(10)	1·546 (6)	C(21)–O(22)	1·204 (6)
N(7)–C(8)	1·480 (6)	C(21)–O(23)	1·361 (6)
N(7)–C(11)	1·532 (6)	O(23)–C(24)	1·454 (6)
N(7)–B(25)	1·623 (6)		

C(2)–N(1)–C(20)	108·7 (3)	C(15)–C(10)–C(2)	100·3 (4)
C(3)–C(2)–C(10)	124·8 (4)	C(15)–C(10)–C(6)	119·6 (4)
C(3)–C(2)–N(1)	129·3 (4)	C(15)–C(10)–C(9)	108·9 (4)
C(10)–C(2)–N(1)	105·4 (4)	C(2)–C(10)–C(6)	112·0 (4)
C(4)–C(3)–C(21)	121·9 (4)	C(2)–C(10)–C(9)	112·0 (4)
C(4)–C(3)–C(2)	118·7 (4)	C(6)–C(10)–C(9)	104·4 (3)
C(21)–C(3)–C(2)	117·9 (4)	C(12)–C(11)–N(7)	114·3 (4)
C(5)–C(4)–C(12)	106·8 (4)	C(4)–C(12)–C(11)	111·3 (4)
C(5)–C(4)–C(3)	109·2 (4)	C(14)–C(13)–C(5)	127·6 (5)
C(12)–C(4)–C(3)	116·0 (4)	C(16)–C(15)–C(20)	120·8 (4)
C(6)–C(5)–C(13)	122·5 (4)	C(16)–C(15)–C(10)	131·8 (4)
C(6)–C(5)–C(4)	110·1 (4)	C(20)–C(15)–C(10)	107·2 (4)
C(13)–C(5)–C(4)	127·5 (4)	C(17)–C(16)–C(15)	116·8 (5)
N(7)–C(6)–C(10)	105·3 (3)	C(18)–C(17)–C(16)	121·5 (5)
N(7)–C(6)–C(5)	112·2 (3)	C(19)–C(18)–C(17)	122·2 (5)
C(10)–C(6)–C(5)	113·3 (3)	C(20)–C(19)–C(18)	116·4 (4)
C(8)–N(7)–C(11)	106·5 (3)	N(1)–C(20)–C(15)	109·0 (4)
C(8)–N(7)–B(25)	111·4 (4)	N(1)–C(20)–C(19)	128·6 (4)
C(8)–N(7)–C(6)	102·6 (3)	C(15)–C(20)–C(19)	122·3 (4)
C(11)–N(7)–B(25)	110·8 (3)	O(22)–C(21)–O(23)	122·1 (4)
C(11)–N(7)–C(6)	111·9 (3)	O(22)–C(21)–C(3)	125·7 (4)
B(25)–N(7)–C(6)	113·3 (3)	O(23)–C(21)–C(3)	112·2 (4)
C(9)–C(8)–N(7)	106·1 (4)	C(24)–O(23)–C(21)	115·4 (4)
C(10)–C(9)–C(8)	104·3 (4)		

in Fig. 2. There are no short intermolecular contacts that would appear to influence greatly the molecular conformation. The shortest contact involving the B atom is 3·72 Å with C(8) in the molecule at $\frac{1}{2}+x$, $1\frac{1}{2}-y$, $1-z$.

This analysis emphasizes the desirability for careful chemical and spectral characterization of the material being studied and for the need to reconcile any inconsistencies between the observed structural and anticipated chemical results.

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