

sulphide and 1.94 Å in tetraethyl diphosphine disulphide. The bond angle S-P-P' of 111.1° compares with 112° in dimethyl diphenyl diphosphine disulphide and 113° in tetraethyl diphosphine disulphide.

Table 6. *Bond lengths and their standard deviations*

Bond	Distance	σ
P—P'	2.21 Å	0.004 Å
S—P	1.95	0.002
P—C(1)	1.82	0.007
P—C(4)	1.82	0.007
C(1)—C(2)	1.52	0.011
C(3)—C(4)	1.51	0.010
C(2)—C(3)	1.52	0.015

Table 7. *Bond angles and their standard deviations*

	Angle	σ
S—P—C(1)	118.7°	0.3°
S—P—C(4)	116.5	0.3
S—P—P'	111.1	0.1
C(1)—P—P'	105.5	0.1
C(4)—P—P'	107.0	0.1
C(1)—P—C(4)	96.6	0.3
P—C(1)—C(2)	104.6	0.5
P—C(4)—C(3)	105.1	0.6
C(1)—C(2)—C(3)	108.5	0.8
C(2)—C(3)—C(4)	108.8	0.7

The bond lengths and angles in the ring show a regular arrangement. The P-C distances, both of 1.82 Å, are close to the values of 1.82 Å in dimethyl diphenyl diphosphine disulphide and of 1.82 and 1.84 Å in tetraethyl diphosphine disulphide. These values are in close agreement with the value of 1.84 Å obtained from the sum of Pauling's (1960) single bond covalent radii. The ring system is saturated and is consequently puck-

ered, and the bond angles round the carbon atoms are slightly less than the usual tetrahedral value. The inclusion of phosphorus in a heterocyclic ring causes considerable distortion of the tetrahedral environment round the phosphorus, and the bond angle C(1)-P-C(4) is 96.6°. It is surprising that this has no observable effect on the bond order of the P-P and P=S bonds. A large number of intermolecular contacts occur in the range 3.85–4.0 Å, but there are no intermolecular contacts below 3.85 Å except those involving hydrogen atoms.

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The Crystal Structure and Absolute Configuration of the *N(b)*-Methiodide of (–)-Kopsanone

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Crystals of the *N(b)*-methiodide of the indole alkaloid (–)-kopsanone, [C₂₁H₂₅N₂O]⁺I[–], are orthorhombic with lattice translations $a=13.98$, $b=17.20$, $c=7.67$ Å, space group $P2_12_12_1$, four formula units per unit cell. The crystal structure has been determined from 1800 three-dimensional X-ray intensity data, collected with an automatic four-circle diffractometer, the absolute configuration being established from the Cu $K\alpha$ anomalous scattering of the iodide ion. Refinement of positional and isotropic temperature factors was by full-matrix least-squares, giving convergence at $R=0.08$. Hydrogen atom positions were not determined. The results confirm the molecular structure previously proposed on the basis of chemical and spectral data. The heptacyclic molecular structure has a cage-like aliphatic portion, with the piperidine ring *D* in the chair form. The conformation of the remainder of the molecule and of (–)-kopsanone itself follows from the interlocking nature of the ring fusions.

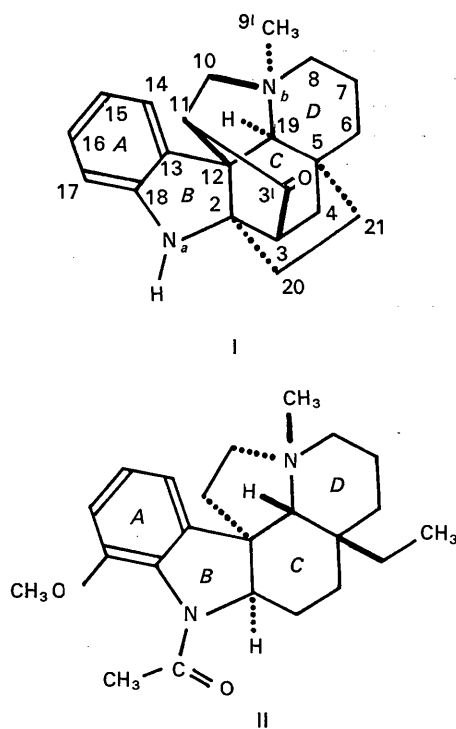
Introduction

Several families of indole alkaloids with similar molecular structures have been isolated from *Aspidosperma*,

Pleiocarpa, *Kopsia* and other genera. The chemistry of these alkaloids has been reviewed by Gilbert (1965). In considering their structural and biosynthetic relationships, (–)-kopsanone is important since it has been

isolated from two different genera (*Aspidosperma duckei* Hub., *A. macrocarpon* Mart, *Pleiolepta muticosa* Benth; Ferreira Filho, Gilbert, Kitagawa, Paes Leme & Durham, 1966; Achenbach & Biemann, 1965) and possesses the heptacyclic skeleton of kopsine and other alkaloids which have been isolated from yet a third genus (*Kopsia*). Kopsanone has also been obtained by pyrolysis of kopsinic acid (Kump, Dugan & Schmid, 1966).

This paper concerns the crystal structure and absolute configuration of the *N(b)*-methiodide of (-)-kopsanone (I).^{*} The results have already been reported briefly (Craven, Gilbert & Paes Leme, 1968).



Experimental

Crystals of kopsanone *N(b)*-methiodide were supplied by Drs Gilbert and Paes Leme of the Federal University of Rio de Janeiro, Brazil. The crystals are orthorhombic

^{*} The atomic nomenclature in (I) conforms with Gilbert (1965).

with lattice parameters $a=13.98 \pm 0.005$, $b=17.20 \pm 0.05$ and $c=7.67 \pm 0.02$ Å, and space group $P2_12_12_1$. The crystal density of 1.62 g.cm^{-3} , measured by flotation

Table 2. Atomic parameters with *e.s.d.*'s

The positional parameters are expressed as fractions of the lattice translations.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	$B, \sigma(B)$
I	0.66765	0.78901	0.8632	3.69 Å ²
N(a)	0.00007	0.00006	0.0001	0.03
	0.4949	0.4393	0.479	3.4
N(b)	0.0010	0.0008	0.002	0.2
	0.5157	0.7084	0.403	2.6
O	0.0008	0.0007	0.001	0.2
	0.3504	0.5159	0.146	4.7
	0.0009	0.0007	0.002	0.2
C(2)	0.4541	0.5100	0.542	3.1
	0.0011	0.0009	0.002	0.3
C(3)	0.3575	0.5321	0.460	3.3
	0.0011	0.0009	0.002	0.3
C(3')	0.3899	0.5416	0.271	3.4
	0.0012	0.0009	0.002	0.3
C(4)	0.3252	0.6099	0.537	3.5
	0.0011	0.0009	0.002	0.3
C(5)	0.4060	0.6512	0.643	2.9
	0.0010	0.0008	0.002	0.2
C(6)	0.3821	0.7339	0.694	4.3
	0.0013	0.0010	0.003	0.3
C(7)	0.3769	0.7847	0.540	4.5
	0.0013	0.0011	0.003	0.3
C(8)	0.4761	0.7901	0.452	3.4
	0.0011	0.0009	0.002	0.3
C(9')	0.6191	0.7216	0.359	3.3
	0.0010	0.0008	0.002	0.3
C(10)	0.4677	0.6726	0.249	3.2
	0.0011	0.0009	0.002	0.3
C(11)	0.4841	0.5846	0.274	2.5
	0.0010	0.0008	0.002	0.2
C(12)	0.5214	0.5724	0.464	2.7
	0.0010	0.0008	0.002	0.2
C(13)	0.6161	0.5291	0.481	2.9
	0.0011	0.0008	0.002	0.3
C(14)	0.7116	0.5536	0.506	3.5
	0.0011	0.0009	0.002	0.3
C(15)	0.7847	0.4976	0.506	4.2
	0.0013	0.0011	0.003	0.3
C(16)	0.7651	0.4213	0.491	4.7
	0.0014	0.0011	0.003	0.4
C(17)	0.6668	0.3944	0.478	4.0
	0.0013	0.0009	0.002	0.3
C(18)	0.5977	0.4517	0.477	3.3
	0.0011	0.0009	0.002	0.3
C(19)	0.5070	0.6518	0.554	2.8
	0.0010	0.0008	0.002	0.2
C(20)	0.4251	0.6001	0.803	4.3
	0.0013	0.0011	0.003	0.3
C(21)	0.4476	0.5160	0.747	3.7
	0.0013	0.0010	0.002	0.3

Table 1. Refinement criteria

Criteria	1st refinement (enantiomer of true structure)	2nd refinement (true structure)
Standard deviation in an observation of unit weight	0.75	0.58
<i>R</i> index, all data	0.106	0.081
<i>R</i> index, omitting unobserved	0.102	0.077
Weighted <i>R</i> index, all data	0.131	0.100
Weighted <i>R</i> index, omitting unobserved	0.125	0.097

Table 3. Observed and calculated structure factors
The columns listed are k, 10|F_o|, 10|F_c|, 10A_c, 10B_c.

Table with multiple columns containing numerical data for structure factors. The table is organized into several vertical sections, each with its own set of column headers. The data includes observed and calculated values for various reflections, with some cells containing additional identifiers like 'L' or 'H'.

Table 3 (cont.)

Table with multiple columns of numerical data, likely representing diffraction intensity measurements. The table is organized into several vertical sections, each with its own set of column headers. The data points are arranged in rows, showing various intensity values across different indices.

Table 3 (cont.)

Table with multiple columns of numerical data, continuing the diffraction intensity measurements from the first table. It follows the same multi-column layout and contains a similar range of intensity values.

sisting of all reflections with $\sin \theta/\lambda < 0.59 \text{ \AA}^{-1}$ for which h, k and l were positive with respect to a right-handed crystal axial system. Integrated intensities were obtained from $\theta/2\theta$ scans of 2° in 2θ at a scanning rate of 2° min^{-1} , with background counts of 20 sec at each scan limit. There were 110 reflections for which the integrated intensity, I , was less than $1.5 \sigma(I)$. These were assigned values of I equal to $0.5 \sigma(I)$. As a result of X-irradiation, the crystal slowly turned yellow and showed a uniform overall decrease by ten per cent in the integrated intensities of three standard reflections by the end of the data collection. Scaling factors were applied to compensate for this effect. X-ray absorption factors were not applied.

The determination of the absolute configuration was confirmed by intensity measurements with $\text{Cu K}\alpha$ radiation made with the use of a second crystal, similar in size to the first, but with a shape closely approximating mmm symmetry in order to minimize differences in the X-ray absorption factors for the Bijvoet pairs. Integrated intensities of reflections $hkl, \bar{h}\bar{k}l$ of form $\{hkl\}$ and reflections $h\bar{k}l, \bar{h}kl$ of the form $\{\bar{h}\bar{k}l\}$ were measured. At this time, the crystal structure had been determined and it was considered sufficient to measure two Bijvoet pairs for which the intensity differences $[I(hkl) - I(\bar{h}\bar{k}l)]$ were predicted to be large and of opposite sign and a third pair for which the difference should be small. The results are shown in Table 4.

The structure determination and parameter refinement

The iodide ion positions were determined from the three Harker sections $u = \frac{1}{2}, v = \frac{1}{2}, w = \frac{1}{2}$. All non-hydrogen atoms were recognized in the three-dimensional Fourier synthesis of electron density, by use of the iodide phases.

The atomic positional parameters and isotropic thermal parameters (initially assumed to be 3.5 \AA^2 for all atoms), were refined by a full-matrix least-squares procedure. The atomic scattering factors, including the X-ray dispersion effect for the iodine atoms ($\Delta f' = -1.2 \Delta f'' = 7.0$ for $\text{Cu K}\alpha$ radiation) were taken from *International Tables for X-ray Crystallography* (1962). The estimated standard deviation in an observed structure amplitude, $|F|$, was assumed to be

a four-circle automatic diffractometer. With $\text{Cu K}\alpha$ radiation and a scintillation counter detector, 1800 non-symmetry related reflections were measured, con-

$$\sigma(F) = |F_{\min}| + 0.07|F|,$$

where $|F_{\min}|$ is the average value of the structure amplitude assigned to unobservably weak reflections.

The criteria of the refinement process are shown in Table 1. The first refinement converged after three cycles of least squares. The atomic positional parameters were then inverted with respect to the crystallographic origin, and the resulting enantiomeric structural parameters were then refined with an additional two cycles. The improved agreement between calculated and observed structure factors in the second refinement suggests that these parameters, when referred to a right-handed set of crystal axes, correspond to the correct absolute configuration. This absolute configuration was confirmed by comparison of the observed and calculated intensity differences $[I(hkl) - I(\bar{h}\bar{k}\bar{l})]$ as shown in Table 4. The final atomic parameters with e.s.d.'s from the second refinement are listed in Table 2. The corresponding observed and calculated structure factors are listed in Table 3. A three-dimensional electron density difference map was calculated, with the use of the atomic parameters shown in Table 2. The most prominent features in this map were at the iodine atom position. These could be interpreted as the effects of anisotropic thermal motion of the iodine atom with perhaps some contribution from systematic errors in the intensity data arising from progressive radiation damage in the crystal. Hydrogen atom positions were not determined.

Table 4. Determination of absolute configuration

<i>h</i>	<i>k</i>	<i>l</i>	$(I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}) / I_{hkl}$	
			calc.*	obs.
1	1	1	+0.27	+0.22
1	3	3	-0.17	-0.25
9	1	2	+0.02	+0.02

* These values are based on the atomic parameters listed in Table 2, referred to a right-handed crystal axial system.

Description of the structure

The bond lengths and angles within the molecule are listed in Table 5. These may be referred to the molecular framework shown in Fig. 1. Calculation of best least-squares planes (Table 6) shows that both rings *A* and *B* of the dihydroindole moiety are distorted from planarity as a result of the steric requirements of fusion with the cage-like aliphatic part of the molecule. In ring *A*, only atom C(13) is significantly out of plane. The five-membered ring *B*, containing nitrogen atom N(*a*) is approximately in the envelope form, with atom C(2) at the flap position A similar conformation is found for the cyclopentanone ring, in which the carbon atom C(2) is again at the flap position. The atoms of the carbonyl group and the two adjacent carbon atoms are coplanar (Table 6). The ring junctions in this molecule are all *cisoid*. Furthermore, all rings share three edges with other rings, except for rings *B* and *D*, which

share only two, and ring *A*, which shares only one. The molecule is thus rigid, except for ring *D*, which could reasonably be expected to be in either the chair or skew-boat conformation (Eliel, Allinger, Angyal & Morrison, 1965). The chair conformation is observed.

The packing in the crystal structure is shown in Fig. 2. A notable feature is the overlap of the aromatic rings *A*, which lie close to the planes $z=0, \frac{1}{2}$. It might be supposed that this would be an attractive interaction of some importance in the crystal structure. However, the separation of aromatic ring planes ($c/2$ or 3.83 Å) is considerably greater than the van der Waals separation (3.4 Å) as a result of the packing requirements of the bulky cage-like aliphatic portion of the molecule. Observed intermolecular distances are listed in Table 7.

Each iodide ion is enclosed so that it is within a 5 Å distance of twenty-seven atoms from eight different molecular ions. The shortest of these distances (3.65 Å) is to a nitrogen atom N(*a*) along a line which is approximately in the expected direction for the N(*a*)-H bond. This distance is considerably shorter than the sum (4.3 Å) of the N-H bond length (assuming a value of 0.9 Å), the van der Waals radius for hydrogen (1.2 Å), and the ionic radius for iodine (2.2 Å). Thus, even allowing for some non-collinearity of the atoms N(*a*)-H...I⁻, there is evidence of an attractive interaction, which might be called a hydrogen bond. In the crystal structures of the *N(b)*-methiodide of the alkaloid cleavamine (Cameran & Trotter, 1964) and also in hexamminecobalt(III) triiodide (Barnet, Craven, Freeman, Kime & Ibers, 1966) there are even shorter N-H...I⁻ distances (3.41, 3.46 Å, respectively) although in these cases also, the hydrogen atom positions were not experimentally determined.

In kopsanone methiodide, there are no significant dipole-dipole interactions between carbonyl groups similar to those described by Bolton (1964). The C...O

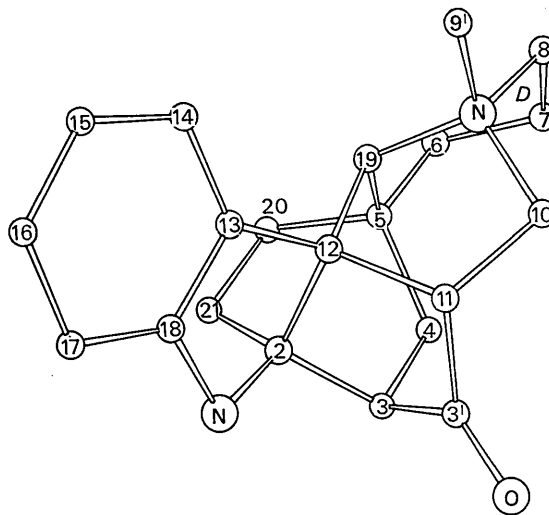


Fig. 1. Molecular framework of the kopsanone ion, showing the absolute configuration.

Table 5(a). *Bond lengths and angles*

The average e.s.d.'s in bond lengths and angles are 0.02 Å and 1.5° respectively.

(a) Bond lengths					
N(a)—C(2)	1.43 Å	C(5)—C(19)	1.57 Å	C(12)—C(13)	1.52 Å
C(2)—C(3)	1.54	C(5)—C(20)	1.53	C(12)—C(19)	1.54
C(2)—C(12)	1.55	C(6)—C(7)	1.47	C(13)—C(14)	1.41
C(2)—C(21)	1.58	C(7)—C(8)	1.55	C(13)—C(18)	1.36
C(3)—C(3')	1.53	C(8)—N(b)	1.56	C(14)—C(15)	1.40
C(3)—C(4)	1.53	N(b)—C(9')	1.50	C(15)—C(16)	1.35
C(3')—O	1.19	N(b)—C(10)	1.49	C(16)—C(17)	1.45
C(3')—C(11)	1.51	N(b)—C(19)	1.52	C(17)—C(18)	1.38
C(4)—C(5)	1.56	C(10)—C(11)	1.54	C(18)—N(a)	1.45
C(5)—C(6)	1.51	C(11)—C(12)	1.56	C(20)—C(21)	1.54

Table 5(b) *Bond lengths averaged according to bond type*

Trigonally and tetrahedrally bonded atoms are denoted by 'trig' and 'tetr'.

Type	No. of bonds	Average bond length	R.m.s. deviation
C(tetr)—C(tetr)	14	1.54 Å	0.007 Å
C(tetr)—C(trig)	3	1.52	0.005
C(trig)—C(trig)	6	1.40	0.015
N(tetr)—C(tetr)	4	1.52	0.014

(c) Bond angles					
C(18)—N(a)—C(2)	106°	C(6)—C(5)—C(19)	108°	C(11)—C(12)—C(19)	105°
N(a)—C(2)—C(3)	115	C(6)—C(5)—C(20)	112	C(2)—C(12)—C(13)	99
N(a)—C(2)—C(12)	103	C(19)—C(5)—C(20)	101	C(2)—C(12)—C(19)	111
N(a)—C(2)—C(21)	115	C(5)—C(6)—C(7)	111	C(13)—C(12)—C(19)	120
C(3)—C(2)—C(12)	102	C(6)—C(7)—C(8)	110	C(12)—C(13)—C(14)	134
C(3)—C(2)—C(21)	110	N(b)—C(8)—C(7)	112	C(12)—C(13)—C(18)	108
C(12)—C(2)—C(21)	112	C(8)—N(b)—C(9')	105	C(14)—C(13)—C(18)	118
C(2)—C(3)—C(3')	99	C(8)—N(b)—C(10)	114	C(13)—C(14)—C(15)	119
C(2)—C(3)—C(4)	108	C(8)—N(b)—C(19)	112	C(14)—C(15)—C(16)	121
C(3')—C(3)—C(4)	112	C(9')—N(b)—C(10)	109	C(15)—C(16)—C(17)	121
C(3)—C(3')—C(11)	107	C(9')—N(b)—C(19)	110	C(16)—C(17)—C(18)	116
C(3)—C(3')—O	126	C(10)—N(b)—C(19)	108	C(17)—C(18)—C(13)	124
C(11)—C(3')—O	127	N(b)—C(10)—C(11)	104	C(17)—C(18)—N(a)	121
C(3)—C(4)—C(5)	113	C(10)—C(11)—C(3')	110	C(13)—C(18)—N(a)	109
C(4)—C(5)—C(6)	114	C(10)—C(11)—C(12)	107	C(5)—C(19)—N(b)	114
C(4)—C(5)—C(19)	115	C(3')—C(11)—C(12)	104	C(5)—C(19)—C(12)	108
C(4)—C(5)—C(20)	106	C(11)—C(12)—C(2)	105	N(b)—C(19)—C(12)	103
		C(11)—C(12)—C(13)	116	C(5)—C(20)—C(21)	110
				C(20)—C(21)—C(2)	111

Table 6. *Best least-squares planes*

(i) Equations of the planes

The equations of these planes are in the form $AX + BY + CZ = D$, referred to the crystallographic axes, with X, Y, Z in Å units.

Plane 1: atoms of the benzene ring, except for C(13).

Plane 2: atoms of the carbonyl group, with adjacent atoms.

Plane	A	B	C	D
1	-0.06137	-0.06663	0.99588	2.61843
2	-0.50219	0.86129	-0.07732	5.10548

(ii) Distances of atoms from the planes

For each plane, column (a) lists distances from the plane of atoms which form the plane, and column (b) lists distances from the plane of atoms which do not form the plane. The e.s.d. in these distances is approximately 0.015 Å.

Plane (1)				Plane (2)			
(a)		(b)		(a)		(b)	
C(14)	-0.00 Å	N(a)	0.11 Å	C(11)	-0.01 Å	C(12)	-0.56 Å
C(15)	0.01	C(13)	-0.08	C(3')	0.02	C(2)	-1.06
C(16)	-0.01	C(12)	-0.18	C(3)	-0.01		
C(17)	0.01	C(2)	0.54	O	-0.01		
C(18)	-0.00						

intermolecular distance is long (4.53 Å), although in Fig. 2 the projected distance is deceptively short.

Discussion

The present crystal structure determination of the *N(b)*-methiodide confirms the molecular structure for (-)-kopsanone determined from chemical and spectral data (Ferreira Filho *et al.*, 1966; Kump, *et al.*, 1966) and the absolute configuration which was proposed on the basis of a chemical correlation with minovincine (Kump *et al.*, 1966).

The determination of absolute configuration is of more than usual importance for *Aspidosperma* and related alkaloids, because of the existence of naturally occurring enantiomeric molecular structures. Quebrachamine and pyrrolidine are among those *Aspidosperma* alkaloids for which enantiomers have been isolated from different plant sources (see references given by Djerassi, Archer, George, Gilbert & Antonaccio, 1961). Wenkert (1962) has suggested mechanisms for indole alkaloid biosynthesis that involve a non-asymmetric intermediate. Although this can explain the observed enantiomerism, the conditions which result in the occurrence of a particular enantiomer in a particular plant are not yet understood.

From chemical and optical rotatory dispersion data, assignments of absolute configuration have been made (Klyne, Swan, Bycroft, Schumann & Schmid, 1965), which may be extended to include most of the known *Aspidosperma* and related alkaloids. However, except

in the present case and in the recent work on the *N(b)*-methiodide of (-)-aspidospermine* (Craven & Zacharias, 1968), the X-ray anomalous scattering method has not previously been used to determine the absolute configuration of an alkaloid closely related to the naturally occurring *Aspidosperma* series. These X-ray results confirm the previous assignments in showing that, except at carbon atom C(2), the *N(b)*-methiodides of (-)-kopsanone (I) and (-)-aspidospermine (II) have opposite configurations at each of the five asymmetric centers which they have in common. The difference in absolute configuration at carbon atom C(2) in (-)-kopsanone with respect to (+)-aspidospermine indicates that these compounds may be related by the cyclization at atom C(2) of the ethyl substituents at carbon atom C(5) in the latter compound.

Smith & Wrobel (1960) have given some evidence that the conformation of aspidospermine is different from that which is observed in the crystal structure of the *N(b)*-methiodide (Mills & Nyburg, 1960) and that the *N*-methylation reaction of aspidospermine involves an 'umbrella'-type inversion of configuration about the nitrogen atom *N(b)*. Such behaviour is unlikely in the case of kopsanone because of the rigidity of the cage-like aliphatic portion of the molecule. Three of the bonds in the piperidine ring *D* are locked in positions so that flexing of this ring in the process of nitrogen atom inversion involves considerable angular strain. The de-

* The crystal structure was reported by Mills & Nyburg (1960), but the absolute configuration was not determined.

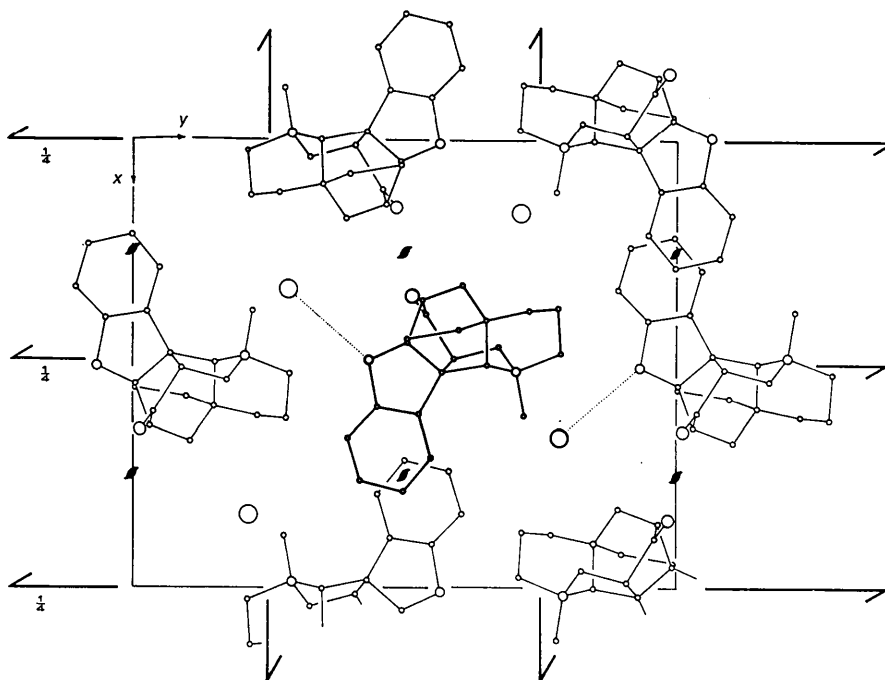


Fig. 2. The crystal structure of kopsanone *N(b)*-methiodide. The positive sense of the crystal axis *c* is towards the viewer. The atomic parameters of Table 2 refer to the molecule in the center. The presumed *N(a)H*···*I*⁻ hydrogen bonds are shown as dotted lines.

Table 7. *Intermolecular distances*

The interatomic distances listed include all those which are less than 0.2 Å in excess of the sum of the appropriate ionic or van der Waals radii (2.2 Å for I⁻, 2.0 Å for tetrahedrally bonded carbon, 1.7 Å for trigonally bonded carbon, 1.4 Å for oxygen; Pauling, 1960). Distances which are long by this criterion are indicated by *.

Subscripts (*a, b, c, ...*) indicate that the right-hand member of each pair of atoms is related to the atom listed in Table 2 by one of the following symmetry operations:

<i>a</i> :	$1-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$	<i>f</i> :	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
<i>b</i> :	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$1-z$	<i>g</i> :	$-\frac{1}{2}+x$	$\frac{3}{2}-y$	$1-z$
<i>c</i> :	x	y	$1+z$	<i>h</i> :	x	y	$-1+z$
<i>d</i> :	$\frac{3}{2}-x$	$1-y$	$\frac{1}{2}+z$	<i>i</i> :	$\frac{3}{2}-x$	$1-y$	$-\frac{1}{2}+z$
<i>e</i> :	$1-x$	$-\frac{1}{2}+y$	$\frac{3}{2}-z$	<i>j</i> :	$\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$

I ⁻ ·····N(<i>a</i>) _{<i>a</i>}	3.65 Å (hydrogen bond)	N(<i>a</i>)·····I ⁻	3.65 (hydrogen bond)
·····C(3) _{<i>a</i>}	4.40	C(2)·····I ⁻ _{<i>e</i>}	4.22*
·····C(4) _{<i>b</i>}	4.16	C(3)·····O _{<i>f</i>}	3.34*
·····C(6)	4.30	·····I _{<i>e</i>} ⁻	4.40
·····C(8)	4.14	C(3')·····C(20) _{<i>h</i>}	3.76
·····N(<i>b</i>)	4.34	·····C(21) _{<i>h</i>}	4.12*
·····C(9') _{<i>c</i>}	4.03	C(4)·····O _{<i>f</i>}	3.38
·····C(9')	4.09	·····I _{<i>e</i>} ⁻	4.16
·····C(10) _{<i>b</i>}	4.33	C(6)·····C(9') _{<i>g</i>}	3.78
·····C(16) _{<i>d</i>}	3.86	·····C(17) _{<i>a</i>}	3.80
·····C(17) _{<i>d</i>}	4.01	·····I ⁻	4.30
·····C(19)	4.03	C(7)·····C(9') _{<i>g</i>}	3.69
·····C(21) _{<i>a</i>}	4.31	·····C(14) _{<i>g</i>}	3.63
C(7)·····C(15) _{<i>g</i>}	3.98	C(16)·····C(14) _{<i>i</i>}	3.76*
C(8)·····I ⁻	4.14	·····C(14) _{<i>d</i>}	3.99*
N(<i>b</i>)·····I ⁻	4.34	·····C(15) _{<i>i</i>}	4.03*
C(9)·····C(6) _{<i>b</i>}	3.78	·····I _{<i>e</i>} ⁻	3.86
·····C(7) _{<i>b</i>}	3.69	C(17)·····C(6) _{<i>e</i>}	3.79
·····I _{<i>h</i>} ⁻	4.03	·····I _{<i>e</i>} ⁻	4.01
·····I ⁻	4.09	C(18)·····C(15) _{<i>i</i>}	4.06*
C(10)·····C(20) _{<i>h</i>}	3.69	C(19)·····C(16) _{<i>d</i>}	4.79*
·····I _{<i>g</i>} ⁻	4.33	·····I ⁻	4.03
C(11)·····C(20) _{<i>h</i>}	3.71	C(20)·····C(3') _{<i>c</i>}	3.76
·····C(21) _{<i>h</i>}	4.24*	·····C(10) _{<i>e</i>}	3.69
C(13)·····C(15) _{<i>d</i>}	3.92*	·····C(11) _{<i>c</i>}	3.71
C(14)·····C(7) _{<i>b</i>}	3.63	·····O _{<i>c</i>}	3.18
·····C(15) _{<i>i</i>}	3.93*	C(21)·····C(11) _{<i>c</i>}	4.24*
·····C(15) _{<i>d</i>}	3.94*	·····O _{<i>c</i>}	3.35
·····C(16) _{<i>d</i>}	3.76*	O·····C(3) _{<i>j</i>}	3.34*
C(15)·····C(13) _{<i>d</i>}	3.92*	·····C(4) _{<i>j</i>}	3.38
·····C(14) _{<i>i</i>}	3.94*	·····C(20) _{<i>h</i>}	3.18
·····C(14) _{<i>d</i>}	3.93*	·····C(21) _{<i>h</i>}	3.35
·····C(15) _{<i>i</i>}	3.96*		
·····C(15) _{<i>d</i>}	3.96*		
·····C(16) _{<i>d</i>}	4.03*		

tailed conformation of (-)-kopsanone thus follows from that of the *N(b)*-methiodide, as described in the previous section and as shown in Fig. 1.

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