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A New Polytype of Silicon Carbide, 57*R*. Its Structure and Growth

By P. Krishna* and Ajit Ram Verma
Department of Physics, Banaras Hindu University, India

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A 57-layered modification of silicon carbide, having rhombohedral symmetry has been discovered. It is shown to have the structure $(33\ 33\ 34)_3$ in Zhdanov's notation. The close agreement of calculated relative intensities of diffracted X-rays with those observed on a Weissenberg photograph establishes the postulated structure. Its growth is discussed.

Introduction

The interesting property of polytypism is prominently exhibited by silicon carbide, of which over 30 stable modifications have already been discovered, and there appears to be no upper limit to their number. It is still not fully understood how so many modifications form or grow. Explanations have been attempted on the basis of

(i) The impurities present during the process of growth (Zhdanov & Minervina, 1945; Lundqvist, 1948).
(ii) The accretion of polymers of SiC with a stacking reversal inherent in their structure and stability governed by temperature (Ramsdell & Kohn, 1952).
(iii) The influence of a neighbouring crystal with an orientation different from that of the growing crystal (Zhdanov & Minervina, 1945).
(iv) Spiral growth from screw dislocations (Frank, 1951).
(v) Layer transposition caused by vibration entropy (Jagodzinski, 1954).

None of these has been able to explain all the observed features.

The first three theories are unable to explain large polytypes like 141*R*, 594*R*, etc. The screw dislocation mechanism has received a lot of attention and a large amount of experimental work has been done to bring forth evidence in support of it. It easily explains the growth of the (0001) face and the formation of polytypes. Verma (1951, 1952) photographed growth spirals on the (0001) face of some SiC crystals by the use of phase contrast microscopy and measured their step heights by means of multiple-beam-interferometry. The growth steps were found to be simply related to the size of the X-ray unit cell. Though it is one of the important mechanisms causing growth, it has not yet been able to explain several observed facts. Jagodzinski (1954) has questioned it while working out the thermodynamics of layer structures with one dimensional fault-order and has proposed the layer transposition mechanism caused by vibration entropy.

More experimental investigation of SiC structures is necessary to obtain a clear understanding of their growth. In the present work an extensive study was undertaken to isolate SiC structures with large unit cells and study their growth in the light of the above theories. Of the various large polytypes discovered, the 57 layered modification was given particular attention in order to study the $[(33)_n34]_3$ series of structures of which only two other members, 21*R* and 39*R*, are as yet known. We have been able to determine the structure of this new polytype and place it as the largest known member of the $[(33)_n34]_3$ series. The growth of this structure is also discussed.

Experimental details

The specimen in which the new polytype was discovered is a small, light green crystal about 1 × 1·5 × 0·5 mm., with a shining (0001) face which does not show any spiral markings.

Measurements made on a 15°-oscillation photograph taken on a 3 cm. cylindrical camera indicated a 57-layered unit cell with rhombohedral symmetry. Fig. 1 shows the $1,0\cdot l$ row of spots on a *c*-axis oscillation photograph taken with a camera of radius 11·48 cm. using a very narrow, collimated beam of Cu *K* radiation. The rhombohedral symmetry was confirmed by taking an over-exposed oscillation photograph which showed the Laue streak along the zero layer line. The ζ values of the nearest $1,0\cdot l$ spots on either side of this streak are in the ratio of 1:2.

A weak, diffuse and continuous streak can be seen along the $1,0\cdot l$ row of spots. This streak could not be resolved into spots by increasing the camera radius or collimating the X-ray beam further. This indicates a certain random disorder of layers in the crystal. For the structure determination, discrete spots alone have been considered, disregarding the streak. Further, there are some diffuse spots on the streak that do not belong to the 57*R* structure. No regularity was found in these spots, but they might well be the more intense spots of a very large polytype, the other

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* C.S.I.R. Research Fellow.

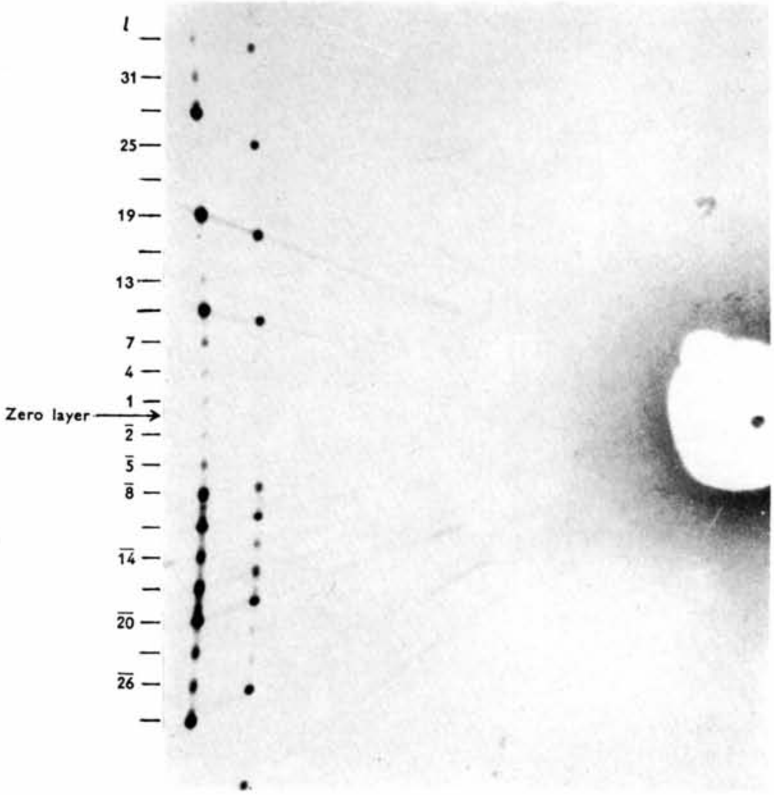

Fig. 1. 15°-oscillation photograph about c-axis, taken with unfiltered Cu K radiation. It shows the 1,0·l row of spots, recorded on a film of radius 11·48 cm. Magnification 1·09:1.

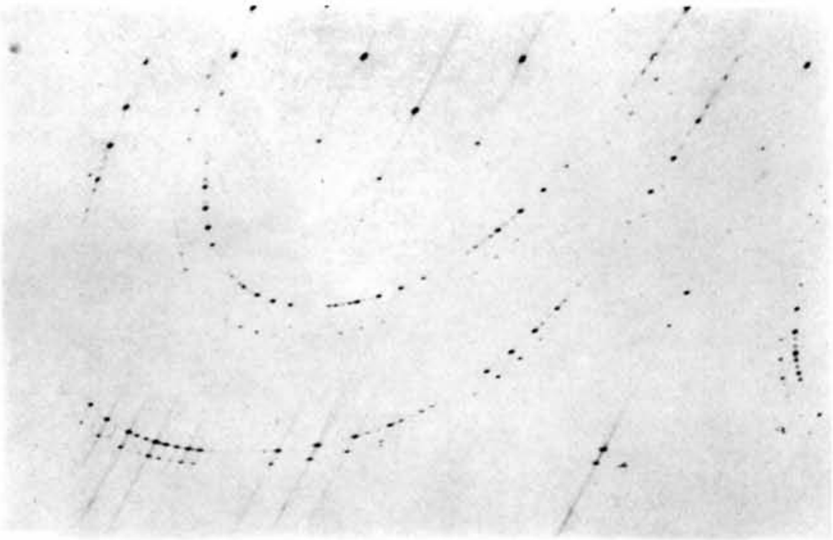

Fig. 2. Zero-layer, a-axis Weissenberg photograph taken with unfiltered Cu K radiation. The lower 'festoon' shows the 1,0·l row of spots. The five consecutive faint spots near the minimum of the 'festoon' are, from left to right, 1,0·$\bar{5}$, 1,0·$\bar{2}$, 1,0·1, 1,0·4 and 1,0·7. The l values of successive spots differ by 3. Magnification 1:1.

unresolved spots of which give rise to the 'continuous' streak.

Fig. 2 shows a zero-layer Weissenberg photograph taken with the crystal rotated about the *a*-axis. The photograph has been indexed on hexagonal axes. The indices show the systematic absences of the space group *R*3*m*.

Structure of the unit cell

We shall assume, with Ramsdell (1944, 1945), Mitchell (1954), and others, that the structure consists of identical layers of atoms spaced successively at intervals of 2·518 Å along the *c*-axis. This assumption is more than amply justified by:

(i) The close agreement of observed and calculated intensities for structures worked out on this basis.
(ii) The *c*-cimension of all unit cells being integral multiples of 2·518 Å* while the *a* and *b* dimensions remain constant in all polytypes.

There are 2^{18} possible ways of stacking the first 19 layers on each other. The positions of the next 38 layers are determined by rhombohedral symmetry. To seek the correct structure from this formidable number by trial and error would be impossible. However, all structures known so far, with the exception of 2H and cubic SiC, have only the numbers 2, 3, and 4 in Ramsdell's zig-zag sequence. Expecting this to hold for the present polytype also and using Zhdanov's notation the problem reduces to finding the ways in which the number 19 can be split into a sum of twos, threes and fours. Since the number of stacking reversals has to be even, the only ways are

(1) $4\times0+3\times3+2\times5$
(2) $4\times1+3\times1+2\times6$
(3) $4\times1+3\times5+2\times0$
(4) $4\times2+3\times3+2\times1$
(5) $4\times3+3\times1+2\times2$

Working out the various permutations possible under each of the above combinations 15 different 57*R* structures are obtained:

(1) $(33322222)_3$ (2) $(33232222)_3$ (3) $(33223222)_3$
(4) $(32322322)_3$ (5) $(43222222)_3$ (6) $(42232222)_3$
(7) $(433333)_3$ (8) $(443332)_3$ (9) $(443323)_3$
(10) $(433432)_3$ (11) $(434323)_3$ (12) $(224443)_3$
(13) $(224434)_3$ (14) $(244243)_3$ (15) $(242434)_3$

These can be easily transformed into the classical *ABC* notation, or the interval sequence, or Nabarro–Frank's stacking operator-sequence.

The Weissenberg and oscillation photographs show that the spots lying nearest to the position of 6H spots are very intense and their relative intensities are similar to those of 6H. Of the structures listed above the 7th is nearest to the 6H phase and was thus thought to be the most probable structure. It is $(333334)_3$ and is thus a member of the $[(33)_n34]_3$ series with $n=2$. A polytype with this structure was predicted by Ramsdell (1947). The interval sequence of the structure is

3242424424242333333

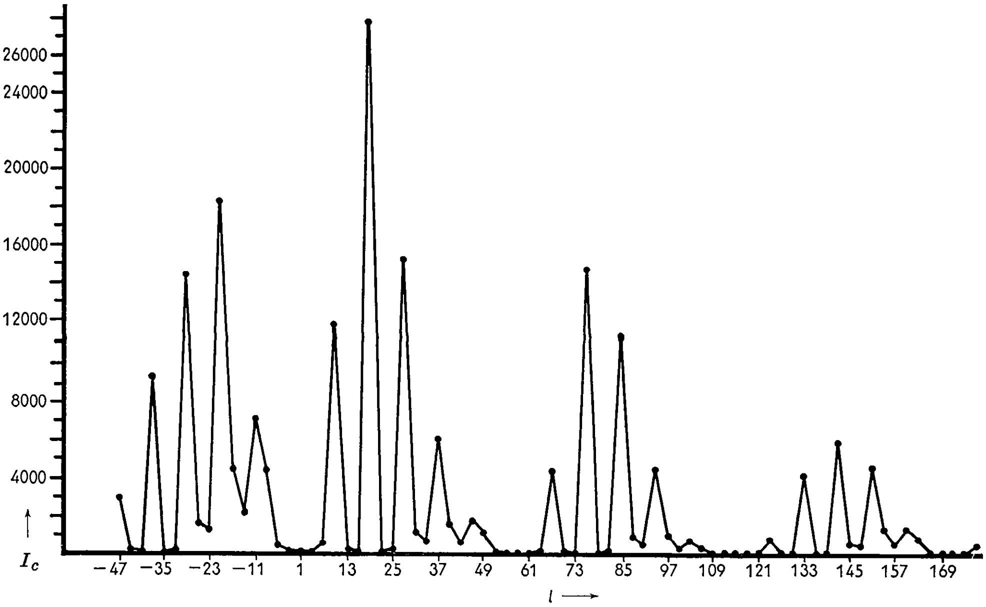

Fig. 3. Graph plotting the calculated relative intensities (I_c) of spots in the 1,0·*l* row against their *l* values, ranging from −47 to +178 at successive intervals of 3.

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* The *c*-dimension of 2*H*, which has been found to be 5·048 Å shows a slight departure from this (Merz & Adamsky, 1959).

Table 1

l	I_c	Observed intensity
1	121	*v. weak*
4	163	*v. weak*
7	548	*weak*
10	11,700	*v. strong*
13	270	*v. weak*
16	91	*v. v. weak*
19	27,730	*v. v. strong*
22	93	*v. v. weak*
25	272	*v. weak*
28	15,190	*v. v. strong*
31	1,214	*strong*
34	681	*weak*
37	6,023	*v. strong*
40	1,590	*strong*
43	527	*weak*
46	1,766	*strong*
49	1,072	*strong*
52	106	*v. v. weak*
55	44	absent
58	36	absent
61	58	absent
64	130	*v. weak*
67	4,403	*v. strong*
70	127	*v. v. weak*
73	43	*v. v. weak*
76	14,620	*v. v. strong*
79	55	*v. v. weak*
82	180	*v. weak*
85	11,090	*v. strong*
88	907	*weak*
91	527	*weak*
94	4,501	*strong*
97	1,024	*weak*
100	270	*v. weak*
103	687	*weak*
106	322	*v. weak*
109	24	absent
112	8	absent
115	9	absent
118	8	absent
121	31	absent
124	797	*weak*
127	23	absent
130	10	absent
133	4,231	*v. strong*
136	20	absent
139	77	*v. v. weak*
142	5,839	*v. strong*
145	579	*weak*
148	428	*weak*
151	4,566	*v. strong*
154	1,301	*strong*
157	429	*weak*
160	1,359	*strong*
163	791	*weak*
166	69	absent
169	27	absent
172	22	absent
175	35	absent
178	395	Not recorded
−2	169	*v. weak*
−5	406	*weak*
−8	4,466	*v. strong*
−11	7,025	*v. strong*
−14	2,007	*strong*
−17	4,460	*v. strong*
−20	18,290	*v. v. strong*
−23	1,354	*strong*
−26	1,627	*strong*
−29	14,320	*v. v. strong*
−32	170	*v. weak*
−35	41	*v. v. weak*
−38	9,303	*v. strong*
−41	26	absent
−44	79	*v. v. weak*
−47	2,941	*strong*

and the *ABC* sequence is

ABCABACBCABACBCABACBCABCBACABCB
ACABCBACABCACBABCACBABCACB.

The variation in intensity of $1,0\cdot l$ spots is very characteristic, and over 75 such spots are recorded on the Weissenberg photograph. As previously established in SiC structure work, an agreement between the observed and calculated intensities for these spots alone suffices to determine the structure. Therefore the calculation of intensities has been done for spots in this row only.

Choosing the origin to lie on a Si atom, the expression for intensity of the $1,0\cdot l$ row of spots for the space group $R3m$ may be written as

$$I \propto \Big[\Big\{\sum_z f_{\mathrm{Si}} \cos 2\pi lz + \sum_z f_c \cos 2\pi l(z+t)\Big\}^2 + \Big\{\sum_z f_c \sin 2\pi l(z+t)\Big\}^2\Big]$$

where $t = 1/76$ is the distance at which C atoms are situated vertically above the Si atoms. The summations have to be done over the following nineteen z-values as obtained readily from the *ABC* sequence of layers:

$$1/57 \times (0, 4, 6, 10, 12, 16, 18, 21, 24, 27, 30, 33, 36, 39, 41, 45, 47, 51, 53).$$

The intensity values calculated from this formula were multiplied by the Lorenz polarization factor $(1+\cos^2 2\theta)/\sin 2\theta$.

Table 1 shows the values obtained for the $1,0\cdot l$ reflections from $l = -47$ to $l = 178$ and the intensity values are plotted to scale against l in Fig. 3. Comparison of the table or graph with the Weissenberg photograph reveals the remarkable extent to which the results match, proving the correctness of the proposed structure. As a check, the intensities for a few typical $1,0\cdot l$ spots were calculated for the other 14 structures. They showed no agreement with observed variations in intensity.

Unit cell dimensions and atomic positions

On hexagonal axes

$$a = 3{\cdot}078,\quad c = 143{\cdot}52_6\ \text{Å};\quad Z = 57\ .$$

The hexagonal unit cell has

19 Si at 000, $00 4z$, $00 6z$, $0,0,10z$, $0,0,12z$, $0,0,16z$, $0,0,18z$, $0,0,21z$, $0,0,24z$, $0,0,27z$, $0,0,30z$, $0,0,33z$, $0,0,36z$, $0,0,39z$, $0,0,41z$, $0,0,45z$, $0,0,47z$, $0,0,51z$, $0,0,53z$,

19 Si at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ plus the above co-ordinates,
19 Si at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ plus the above co-ordinates,

where $z = 1/57$, and

57 C, one above each Si, at a distance
$p = 1/76$ having co-ordinates
$00p$ plus the co-ordinates of the 57 Si atoms.

Discussion of results: Mode of growth

The fact that the arbitrary assumption of the zig-zag sequence not containing any numbers other than 2, 3 or 4 yielded a successful determination of the structure adds further weight to this being a genuine limitation and not merely an accidental feature.* A theoretical explanation for this limitation ought to be provided by some theory of growth.

The formation of this crystal is easily understood, and in fact anticipated by Ramsdell & Kohn's (1952) idea of accretion of polymers. Thus if growth occurred at a temperature at which the polymers 33 and 34 coexist in the proportion of 2:1, then the resulting structure would be $(33\,33\,34)_3$. The continuous streak observed along the $1{,}0{\cdot}l$ row of spots would be explained by the random disorders introduced by the fluctuating conditions in the furnace. But so far, the existence of such polymers, as the theory assumes, has not been experimentally demonstrated.

On the screw dislocation mechanism it is easy to picture the growth of hexagonal structures from a pure screw dislocation. But for the growth of rhombohedral structures a horizontal displacement has to be introduced. This was done by Mitchell (1957) and followed up by Bhide & Verma (1959) in their idea of an inclined dislocation. The mechanism causing this horizontal displacement is not yet understood. We wish to suggest a possible mechanism for the same.

The growth of any structure by the screw dislocation mechanism is really the winding up of the exposed ledge into a very flat spiral whose pitch is the same as the height of the ledge, thus producing a close-packed structure. Any one layer is not really in one plane, but is winding upwards very gradually, so that over fairly large areas (of several unit cell dimensions) any layer might be taken to be in one plane. Hence the structure may also be described by the close packing of plane *A*, *B*, *C* layers, a model that has been used in determining the structure. Now when the first and last layers of an exposed ledge are in different orientations it is easy to picture its winding over itself in a close-packed manner. But this will not be possible if the first and last layers of an exposed ledge are in identical orientation (*A*, *B* or *C*); for then the first layer cannot grow over the last one without slipping the whole stack of layers. Frank (1951) has shown that the layers of the stack shall maintain their interrelationship undisturbed. Thus everytime the stack moves through one pitch there would be a horizontal displacement or slip, shifting the layers of the stack in a cyclic manner ($A \to B$, $B \to C$, $C \to A$ or vice versa). Three such shifts in the same direction would bring the stack back into an identical position, thus creating a structure with a unit cell thrice as high as the exposed ledge. This mechanism implies that rhombohedral structures grow only when the exposed ledge has the first and last layers in the same orientation.

It has been conclusively established (Verma, 1957) from observations of spiral step heights on the (0001) face of 15*R*, 21*R*, 33*R* and 126*R* that the Burgers Vector of the dislocation for rhombohedral structures is only one-third the *c*-dimension of the X-ray unit cell. Thus the screw dislocation creating 57*R* would have a Burgers Vector 19 layers high. There are 6 different ways in which a 19-layered screw dislocation ledge can be exposed in the 6 H structure *ABCACBABCACB*..., but in each case the first and last layers of the exposed ledge are in the same orientation. Consider one such ledge *ABCACBABCACB ABCACBA*. When the first layer tries to grow on the last one it shall slip into a neighbouring site, say *C*, and the next 19 layers would be *CABCBACABCBACA BCBAC*; and again since a *C* layer cannot grow on another *C*-layer, the stack shall slip as before and produce the structure *BCABACBCABACBCABACB*. This time the slip would bring back the ledge into its initial position, thus completing a unit cell with the structure

ABCACBABCACBABCACBA
CABCBACABCBACABCBAC
BCABACBCABACBCABACB,

which has the Zhdanov symbol $(33\,33\,34)_3$.

All rhombohedral structures can be similarly explained to have grown from a ledge, exposed in an initial structure (usually 6*H*, 4*H* or 15*R*), with the first and last layers in the same orientation. A consequence of this idea would be that polytypes belonging to the series $(6n+1)H$ would not be based on the 6*H* phase since a ledge of $(6n+1)$ layers in the 6*H* structure would necessarily have the first and last layers in the same orientation. Indeed the only member of this series so far known is 19*H*, whose structure has been reported by Ramsdell & Mitchell (1953) to be (23232322), based on the 15*R* phase. Similarly polytypes $(4n+1)H$ and $(15n+1)H$ cannot be based on the 4*H* or 15*R* phase respectively. In general, a structure $(pn+1)H$ could not have grown from an initial structure with a *p*-layered unit cell. No structures known so far contradict this.

The screw dislocation mechanism is unable to explain the continuous streak along the $1{,}0{\cdot}l$ row of spots or the random spots obtained in places on the streak. It also does not tell anything about the formation of the initial plate. Only a very few SiC crystals show the spiral markings and that too only on the (0001) face. A single dislocation would produce needle-shaped crystals whereas the observed crystals are usually flat platelets.

Edge dislocations need much less energy for their creation than screw dislocations and would destroy any order created by the screw dislocations (Jagodzinski, 1954). Also a screw dislocation can originate only when the crystal lattice is large enough to provide sufficient energy and so screw dislocations could only cause growth in the later stages. Jagodzinski therefore suggested the layer transposition mechanism caused by vibration entropy. This does explain the continuous

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* The only exceptions known to this rule are 2*H* and cubic SiC structures.

streak so often observed. He has also shown from potential energy considerations that the 15*R* structure is the most stable next to 6*H*, but the question still remains how such extremely improbable structures with large identity periods grow into stable forms.

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The Crystal Structure of α_1-Bromopicrotoxinin

By B. M. Craven

Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania, U.S.A.

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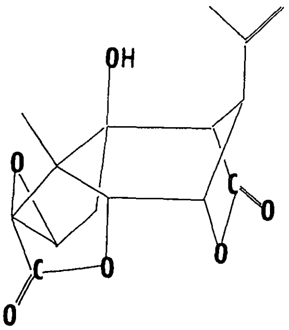
Crystals of α_1-bromopicrotoxinin ($C_{15}H_{15}O_6Br$) are orthorhombic, space group $P2_12_12_1$, with lattice parameters $a = 13{\cdot}40$, $b = 11{\cdot}60$, $c = 8{\cdot}86$ Å, and four molecules in the unit cell. A three-dimensional analysis confirms the structure postulated for picrotoxinin ($C_{15}H_{16}O_6$) by Conroy on chemical evidence. By consideration of the anomalous scattering of X-rays by the bromine atom, the absolute molecular configuration of α_1-bromopicrotoxinin, and hence of picrotoxinin itself, has been established and shown to be the mirror image of the structure as it appears in the previous literature.

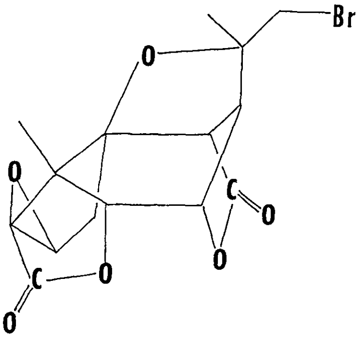
Introduction

Picrotoxinin ($C_{15}H_{16}O_6$) is the physiologically active component which, together with picrotin ($C_{16}H_{18}O_7$) forms the addition compound picrotoxin, a bitter tasting convulsive poison found in the berries of the East Indian creeper, *Anamirta paniculata* and first isolated by Boullay in 1812. These extremely toxic berries have been used by natives to catch fish. Because of its stimulating action on the central nervous system picrotoxin has been used extensively in medicine as an antibarbiturate.

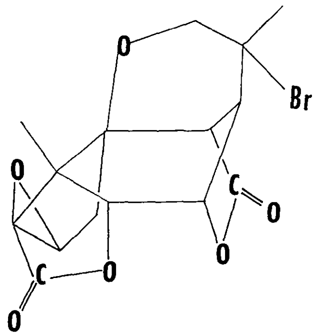
The chemistry of picrotoxinin and picrotin has been a subject of investigations for many years: e.g. by Horrmann (1916), Angelico & Monforte (1923), Robertson, O'Donnel & Harland (1939), Sutter & Schlittler (1949), Slater *et al.* (1956). The structure (I) for picrotoxinin was proposed by Conroy (1951) and subsequently (1957) supported by his conformational analysis.



(I)



(II*a*)



(II*b*)