The use of the SDS form factor for hydrogen has for the most part led to a greater average bond length, as one would hope. The remaining discrepancy between the X-ray and neutron values is less than 2σ in each case (for the mean values of several bond lengths, not for some of the individual values). However the fact that the differences are all in the same direction suggests that the SDS form factor is not adequate to correct fully for the short bond lengths and that it will be necessary to resort to non-spherical scattering factors for precise determination of hydrogen atom positions by X-rays. In the following section, we will use only the neutron diffraction values for hydrogen parameters.

Hydrogen bonding

Hydrogen bonds exist between the base and the chloride ion, between the base and the water molecule, and between the water molecule and chloride ions. The eight N–H···Cl^- hydrogen bonds represent the largest group of this type that has been studied. The interesting hydrogen bond parameters are given in Table 7. In examining this table, the reader should bear in mind that one useful criterion for hydrogen bonding is a hydrogen atom–heavy atom distance that is 0·2 Å or more shorter than the sum of the van der Waals radii (Hamilton & Ibers, 1967). For this purpose we may take the van der Waals radii of H, O, N, and Cl^- as 1·2, 1·4, 1·5, 1·8 Å. The variability in the H···B distances as well as in the A–H···B angles is worthy of note.

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On the Structure of Picrotoxin. II. Direct Determination of the Crystal Structure of β-Bromopicrotoxinin

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The crystal structure of β-bromopicrotoxinin, $C_{15}H_{15}O_6Br$, has been determined from three-dimensional, visually estimated X-ray data by a direct method. The parameters were refined anisotropically by the full-matrix least-squares method. The space group is $P4_3$, $a=b=7{\cdot}14$ Å, $c=28{\cdot}74$ Å. The four molecules in the unit cell are roughly spherical and are placed one on top of the other along the c axis. The molecular geometry is compared to that of the epimeric compound α_1-bromopicrotoxinin, a molecule of which the absolute configuration is already known from the X-ray crystallographic work of Craven [*Acta Cryst.* (1962), **15**, 387].

Introduction

Picrotoxin is a crystalline compound which has found use as a drug in the treatment of barbiturate poisoning. The substance is composed of two molecules, picrotoxinin, $C_{15}H_{16}O_6$, and picrotin, $C_{15}H_{18}O_7$, of which the former is the physiologically active principle. The interest of two of us (BJ & R-J) in the structure of picrotoxin dates back to about 1950, when the molecular structures of the components were still unknown.

Picrotoxin was mostly described in the literature at that time as a simple mixture of the two components, though Sielisch (1912) had already shown without doubt that picrotoxin is a molecular compound of picrotoxinin and picrotin in the molecular ratio 1:1. Hansen & Jerslev (1954) confirmed Sielisch's results by means of a thermal analysis supplemented by X-ray powder photographs of various mixtures of the two compounds of the system picrotoxinin–picrotin. This work also showed that neither of the components is miscible with the molecular compound in the solid state.

BJ & R-J furthermore prepared β-bromopicrotoxinin and collected single-crystal X-ray data of that compound, from which the space group, unit cell and approximate bromine parameters were determined. An unsuccessful attempt was also made to solve the structure from the three-dimensional Patterson function using the superposition method in a graphical way. Since we had no access to electronic computers at that time, and since Craven (1959) in a preliminary note indicated that he was working on the crystal structure of the isomeric α_1-bromopicrotoxinin, we stopped our work on the β compound. A full account of Craven's work giving the molecular structure of α_1-bromopicrotoxinin including the absolute configuration was published subsequently (Craven, 1962).

In 1962, however, one of us (JD) became interested in attempting to solve a non-centrosymmetrical crystal structure by means of direct methods. The present paper describes the result of the work of JD on the above named X-ray data.

It is our intention in due time to try to solve the crystal structure of picrotoxin.

Experimental

β-Bromopicrotoxinin was prepared according to Horrmann (1912) by brominating picrotoxin. Recrystallizations from absolute ethanol gave thin, needle-shaped crystals with a pronounced tendency to split in fibres parallel to the needle axis, melting point (determined under the microscope) 287 °C, destr. Crystals of another habit having m.p. 294 °C, destr. were also seen, apparently an α-isomer. The melting points agree well with the data of Horrmann (1912) and Carman (1963). Weissenberg photographs showed the β-bromopicrotoxinin crystals to be tetragonal, elongated in the **c** direction. $a=b=7{\cdot}11_4$ Å, $c=28{\cdot}7_4$ Å. The density was determined as $1{\cdot}71_5$; the calculated density $1{\cdot}70_2$ gives $Z=4$. Reflexions of all orders were observed except $00l$, which were present only for $l=4$. This, and the Laue symmetry $4/m$, indicate the space group as one of the two enantiomorphs $P4_1$ and $P4_3$. The latter was, after completion of the structure determination, found to be correct. Intensities were registered using Cu $K\alpha$ radiation and multiple-film techniques. The zones $0kl$–$4kl$ were recorded from a crystal fragment of di-

Table 1. *Comparison of theoretical and experimental statistics*

	Centrosymmetry	Non-centrosymmetry	Experimental
$\langle\|E\|^2\rangle$	1·000	1·000	0·985
$\langle\|E\|\rangle$	0·798	0·886	0·898
$\langle\|E^2-1\|\rangle$	0·968	0·736	0·678

Table 2. *Final atomic positions in fractions of the cell edges*

	x	$10^5 \cdot \sigma$	y	$10^5 \cdot \sigma$	z	$10^5 \cdot \sigma$
Br	0·70056	28	0·81447	28	0·59000	—
O(1)	0·80057	169	0·40744	183	0·54561	38
O(2)	0·97430	253	0·27627	239	0·40599	49
O(3)	1·40085	267	0·29017	225	0·40589	59
O(4)	1·35745	183	0·48357	183	0·46599	49
O(5)	1·27206	239	−0·03330	197	0·51819	70
O(6)	1·36728	183	0·25534	169	0·53571	49
C(1)	1·02641	197	0·44775	197	0·48160	49
C(2)	1·21293	225	0·52444	197	0·50110	49
C(3)	1·27079	225	0·43441	197	0·54770	59
C(4)	1·11152	225	0·36686	225	0·57881	49
C(5)	1·05043	225	0·20239	197	0·54940	59
C(6)	0·92388	197	0·30674	211	0·51400	59
C(7)	0·90239	281	0·60028	253	0·46240	70
C(8)	0·91630	225	0·46840	225	0·58529	70
C(9)	0·82458	225	0·39607	267	0·62899	59
C(10)	0·94607	211	0·68062	197	0·58428	70
C(11)	0·82472	295	0·16714	239	0·47968	59
C(12)	0·97852	281	0·14902	267	0·44230	70
C(13)	1·09200	281	0·31489	253	0·44380	59
C(14)	1·29636	267	0·35534	267	0·43498	70
C(15)	1·23315	295	0·12739	225	0·53191	70

mensions $a \times b \times c = 0{\cdot}16 \times 0{\cdot}16 \times 0{\cdot}24$ mm^3. Reflexions $hk0$ were recorded from a crystal fragment with cross section about $0{\cdot}2 \times 0{\cdot}2$ mm^2. The intensities were estimated visually by means of a calibrated scale and converted to a set F_{obs} values in the usual way.

α-Chloropicrotoxinin was prepared in an analogous way, and we confirm Craven's (1959) report, that this substance is isomorphous with the bromine compound. We found m.p. 277 °C, $a=b=7{\cdot}09$ Å, $c=29{\cdot}0$ Å and density = $1{\cdot}50_0$. The calculated density $1{\cdot}49_0$ gives $Z=4$.

Structure determination

The 1247 independent $F^2_{\mathbf{h}_{obs}}$ values were corrected for vibrational motion and placed on an absolute scale by a method described by Hauptman & Karle (1953) and Karle, Hauptman & Christ (1958). These corrected values, $F^2_{\mathbf{h}}$, were converted to normalized structure factors using the relation:

$$E^2_{\mathbf{h}} = F^2_{\mathbf{h}} / (\varepsilon_{\mathbf{h}} \sum_{j=1}^{N} f^2_{j\mathbf{h}}) .$$

Table 3. *Final anisotropic parameters*

Temperature factor expressed as $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}lhc^*a^*+2U_{12}hka^*b^*)]$

	U_{11}	$\sigma(U_{11})$	U_{22}	$\sigma(U_{22})$	U_{33}	$\sigma(U_{33})$	U_{12}	$\sigma(U_{12})$	U_{13}	$\sigma(U_{13})$	U_{23}	$\sigma(U_{23})$
Br	0·066	0·001	0·057	0·001	0·092	0·004	0·006	0·001	0·023	0·001	0·000	0·001
O(1)	0·053	0·006	0·053	0·006	0·046	0·004	−0·010	0·006	0·002	0·005	0·006	0·005
O(2)	0·086	0·010	0·085	0·010	0·046	0·008	−0·019	0·009	−0·018	0·006	−0·012	0·006
O(3)	0·090	0·011	0·061	0·008	0·067	0·008	0·011	0·008	0·031	0·009	−0·015	0·006
O(4)	0·053	0·007	0·050	0·006	0·058	0·008	−0·006	0·006	0·011	0·005	−0·009	0·006
O(5)	0·041	0·007	0·075	0·009	0·125	0·013	−0·002	0·007	−0·015	0·010	−0·038	0·008
O(6)	0·046	0·006	0·041	0·006	0·075	0·008	0·014	0·006	−0·006	0·006	−0·011	0·005
C(1)	0·041	0·007	0·029	0·006	0·029	0·004	0·004	0·006	−0·003	0·005	0·001	0·005
C(2)	0·025	0·006	0·057	0·008	0·042	0·008	−0·012	0·006	0·004	0·006	−0·006	00·05
C(3)	0·040	0·008	0·030	0·006	0·050	0·008	−0·005	0·006	0·008	0·006	−0·011	0·006
C(4)	0·046	0·008	0·046	0·008	0·033	0·008	−0·003	0·006	−0·005	0·005	0·006	0·005
C(5)	0·037	0·008	0·037	0·006	0·050	0·008	−0·003	0·006	0·005	0·006	0·001	0·006
C(6)	0·047	0·008	0·037	0·006	0·050	0·008	−0·010	0·006	0·000	0·006	−0·007	0·007
C(7)	0·065	0·011	0·047	0·009	0·046	0·008	0·013	0·008	−0·005	0·009	0·004	0·007
C(8)	0·047	0·008	0·047	0·008	0·046	0·008	−0·011	0·007	−0·005	0·007	−0·001	0·007
C(9)	0·057	0·010	0·046	0·008	0·046	0·008	−0·001	0·008	0·013	0·006	0·010	0·007
C(10)	0·034	0·007	0·033	0·007	0·063	0·008	0·007	0·006	0·007	0·006	−0·012	0·007
C(11)	0·050	0·008	0·084	0·012	0·050	0·008	−0·019	0·008	−0·003	0·008	−0·012	0·007
C(12)	0·053	0·009	0·052	0·010	0·058	0·008	−0·006	0·009	−0·007	0·008	−0·017	0·008
C(13)	0·059	0·009	0·048	0·009	0·046	0·009	−0·006	0·008	0·004	0·007	−0·007	0·007
C(14)	0·053	0·010	0·050	0·009	0·058	0·008	−0·008	0·008	0·011	0·008	0·002	0·008
C(15)	0·070	0·011	0·023	0·006	0·067	0·008	0·010	0·008	−0·007	0·009	−0·007	0·006

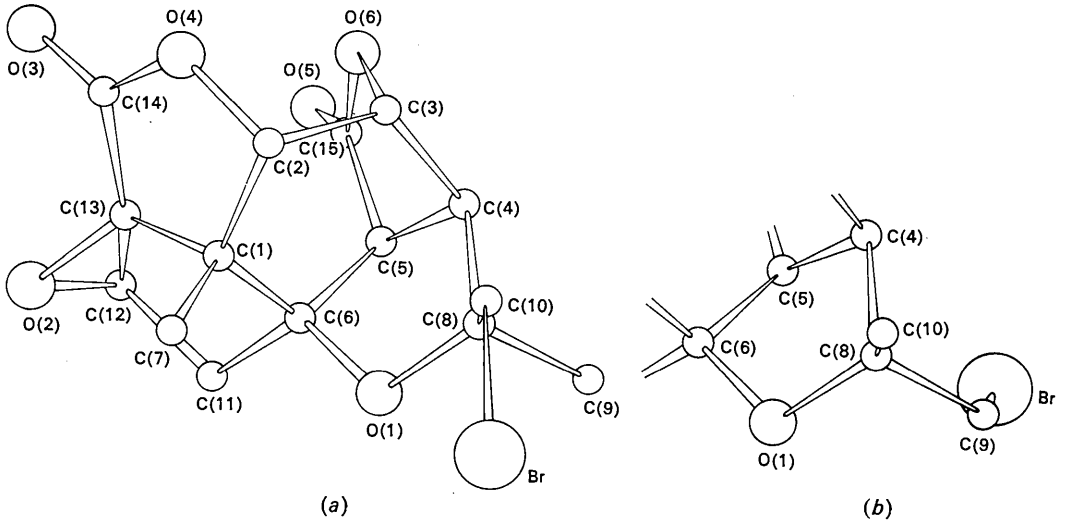

Fig. 1. (*a*) A molecule of β-bromopicrotoxinin viewed along the *b* axis. (*b*) Approximately correct drawing of part of a molecule of α_1-bromopicrotoxinin orientated as the epimeric molecule in (*a*).

N is the total number of atoms in the unit cell, ε_h is a weighting factor; in this case ε_h was set equal to 1, and f_{jh} is the appropriate atomic form factors from *International Tables for X-ray Crystallography*, Vol. III, Table 3.3 1A.

Average values of functions of E_h are compared with the corresponding theoretical values for centrosymmetric and non-centrosymmetric structures in Table 1. It is seen that the choice of the asymmetric space group $P4_1$ is in agreement with the statistics described by *e.g.* Karle, Karle, Owen & Hoard (1965).

From the expression for the joint probability distribution (Naya, Nitta & Oda, 1965) for a set of three structure factors it can be shown that if

Table 4. *Observed and calculated structure factors*

Columns are: index k, $|F_{obs}| \times 10^2$, $|F_{calc}| \times 10^2$, phase angle in millicycles.

0,K,0			
2	1002	965	500
3	275	225	0
4	124	129	0
6	204	148	0
7	3	45	0
8	147	157	500
9	55	51	500
0,K,4			
1	104	120	250
2	879	890	840
3	184	217	663
4	104	105	152
5	55	56	168
6	96	107	488
7	55	50	562
8	147	143	850
9	124	49	932
0,K,8			
1	3	3	894
2	196	199	109
3	347	319	323
4	200	189	114
5	88	105	163
6	257	270	736
7	3	31	152
8	124	137	211
0,K,12			
1	242	258	143
2	375	490	645
3	130	138	112
4	152	159	74
5	257	210	620
6	162	168	25
7	3	27	146
8	96	123	510
0,K,16			
1	78	88	156
2	309	329	986
3	147	172	283
4	124	133	651
5	235	194	785
6	88	91	292
7	39	48	605
8	55	29	902
0,K,20			
1	55	58	774
2	263	283	316
3	39	49	252
4	136	133	38
6	96	97	703
7	39	30	868
0,K,24			
1	88	108	586
2	124	119	663
3	88	87	639
0,K,28			
1	88	88	521
2	55	57	40
3	55	66	302
4	39	38	574
6	55	30	383
0,K,32			
2	55	64	477
3	39	28	771
0,K,2			
1	723	859	479
2	509	526	189
3	883	768	617
4	124	182	733
5	657	570	214
6	117	132	112
7	88	105	847
9	88	31	134
0,K,6			
1	351	304	247
2	737	620	988
3	593	626	53
4	130	108	44
5	419	451	547
6	130	132	564
7	157	167	94
8	39	18	968
0,K,10			
1	312	331	98
2	130	147	525
3	638	580	341
4	88	95	760
5	304	279	831
6	147	154	965
7	117	108	404
8	39	33	385
0,K,14			
1	260	293	296
2	55	62	346
3	316	390	817
4	78	76	678
5	326	337	228
6	242	227	219
7	88	85	696
0,K,18			
1	130	136	646
2	111	131	796
3	387	376	142
4	200	196	326
5	232	201	645
7	55	60	183
0,K,22			
1	68	83	356
2	104	119	247
3	180	181	486
5	104	123	56
0,K,26			
1	78	92	731
2	117	128	85
3	130	128	845
4	78	66	951
5	136	121	274
6	39	27	327
0,K,30			
1	88	95	851
2	78	82	849
3	68	67	178
5	96	86	645
0,K,34			
1	55	58	129
3	55	56	517
0,K,1			
1	329	419	562
2	419	461	217
3	275	274	848
4	166	208	977
5	136	149	838
6	204	194	368
7	147	144	227
0,K,5			
1	816	906	569
2	952	711	765
3	425	436	61
4	573	602	364
5	88	83	252
6	88	93	820
7	232	139	560
8	55	46	594
0,K,9			
1	975	1137	956
2	397	448	231
3	403	386	378
4	487	457	773
5	124	131	629
6	180	194	278
8	78	101	908
0,K,13			
1	487	495	339
2	406	409	536
3	78	98	970
4	525	514	28
5	104	122	344
6	117	97	610
7	78	76	332
8	55	45	252
0,K,17			
1	296	330	633
2	104	102	677
3	111	140	258
4	254	237	335
5	175	197	342
6	136	114	882
7	55	54	589
8	39	14	667
0,K,21			
1	111	112	951
2	200	205	179
3	229	208	445
4	147	152	842
7	55	58	940
0,K,25			
1	215	222	336
2	104	112	518
3	124	130	966
4	55	50	86
6	68	72	763
0,K,29			
1	55	64	825
3	39	54	186
4	68	64	637
0,K,33			
1	39	47	174
4	78	80	850
0,K,3			
1	1075	1247	722
2	750	806	438
3	319	314	121
4	171	223	921
5	204	224	38
6	215	202	275
7	239	237	582
0,K,7			
1	1032	1173	81
2	528	548	717
3	473	487	521
4	408	384	238
5	166	169	227
6	152	158	796
7	104	103	890
8	55	68	116
9	39	77	417
0,K,11			
1	772	699	307
2	263	329	123
3	96	90	700
4	546	509	617
5	200	178	593
6	111	105	93
7	141	120	364
8	39	20	619
0,K,15			
1	291	321	618
2	104	117	224
3	166	166	621
4	393	392	923
5	68	75	164
6	204	206	583
7	88	99	682
8	39	42	751
0,K,19			
1	215	239	75
2	222	242	862
3	147	170	573
4	68	57	30
5	68	74	494
6	88	96	795
7	78	98	996
0,K,23			
1	254	277	499
2	55	66	251
3	55	54	883
4	136	130	583
5	104	84	808
6	55	58	136
7	147	105	297
0,K,27			
1	136	150	996
2	136	133	624
3	39	28	293
5	39	43	254
0,K,31			
1	117	127	73
3	55	47	261
4	39	46	553
1,K,0			
-8	55	69	500
-7	157	222	0
-6	232	224	0
-5	301	279	500
-4	564	645	500
-2	637	615	0
1	629	674	500
2	1014	957	500
3	585	512	0
4	771	710	0
6	211	169	500
7	39	51	0
9	39	10	0
1,K,4			
-8	39	40	660
-7	88	53	576
-6	200	233	397
-5	322	302	834
-4	564	558	799
-3	294	337	375
-2	749	778	337
1	456	452	789
2	848	692	831
3	417	466	316
4	691	647	331
5	39	70	617
6	235	199	957
7	152	117	1
8	68	72	406
9	55	38	289
1,K,8			
-7	141	143	770
-6	257	315	681
-5	204	228	306
-4	543	525	195
-3	280	306	752
-2	152	99	140
1	322	333	297
2	299	261	395
3	111	92	434
4	611	597	712
5	96	122	592
6	344	285	257
7	55	52	879
1,K,12			
-6	291	321	71
-5	329	319	590
-4	162	170	589
-3	329	368	127
-2	136	156	111
1	331	316	490
2	462	454	585
3	78	60	94
4	412	368	103
5	68	79	462
6	184	189	554
7	55	72	105
8	39	43	199
1,K,16			
-8	39	53	180
-7	55	58	408
-6	78	92	281
-5	68	74	886
-4	175	201	11
-3	180	208	295
-2	171	212	587
1	162	156	830
2	524	479	952
3	162	195	267
4	373	356	431
5	39	47	788
6	88	81	938
7	68	68	265
1,K,20			
-7	39	44	901
-6	104	119	833
-5	88	129	320
-4	245	247	283
-3	3	17	39
-2	225	274	825
1	136	150	187
2	111	131	286
3	88	93	811
4	222	196	786
6	55	50	412
7	39	18	413
1,K,24			
-6	55	64	132
-5	55	66	736
-4	157	174	652
-3	96	122	179
-2	204	218	86
1	68	85	520
2	96	101	691
3	180	187	993
4	184	182	193
6	68	78	727
1,K,28			
-5	55	58	73
-4	68	69	954
-2	39	43	568
1	68	71	936
2	111	130	22
4	88	91	512
1,K,32			
-2	68	56	17
1	39	46	58
2	55	52	484
4	68	68	796
1,K,2			
-9	39	48	913
-8	55	66	319
-7	96	110	296
-6	39	53	527
-5	55	40	670
-4	117	121	518
-3	441	471	732
-2	690	714	286
1	1075	1150	627
2	312	334	971
3	294	303	199
4	309	306	558
5	147	134	92
6	55	42	947
7	211	224	717
9	78	64	135
1,K,6			
-8	55	81	510
-7	141	168	566
-6	78	107	97
-5	166	205	994
-4	68	46	299
-3	232	227	913
-2	117	136	539
1	1487	1355	2
2	68	101	547
3	242	241	605
4	222	228	170
5	39	58	296
6	39	47	8
7	248	189	19
1,K,10			
-8	96	111	898
-7	96	100	788
-6	39	52	339
-5	111	101	477
-4	55	88	652
-3	286	350	607
-2	451	451	903
1	502	529	386
2	528	442	950
3	344	322	948
4	294	217	69
5	96	101	19
6	147	134	302
7	192	173	376
8	39	52	572
1,K,14			
-8	39	38	316
-7	55	54	173
-5	366	351	681
-4	235	262	858
-3	192	181	693
-2	289	307	267
1	723	693	784
2	117	113	312
3	239	253	305
4	78	96	822
5	39	41	205
6	55	65	534
7	130	121	716
1,K,18			
-7	55	73	668
-5	68	85	877
-4	175	190	868
-3	157	188	281
-2	242	254	595
1	429	421	128
2	319	307	530
3	136	158	564
4	78	64	34
7	68	72	125
1,K,22			
-5	68	95	212
-4	95	96	753
-3	136	156	489
-2	39	71	876
1	251	274	432
2	111	132	649
3	68	67	113
4	111	103	283
7	111	92	519
1,K,26			
-4	39	49	289
-3	78	88	937
1	88	104	800
2	39	71	548
3	68	70	414
4	68	68	655
5	39	40	574
1,K,30			
-4	39	37	428
-3	39	46	294
-2	88	90	697
1	55	66	288
3	39	47	803
1,K,34			
-3	55	44	696
-2	39	42	222
1	68	67	445
1,K,1			
-9	39	49	803
-8	78	104	864
-7	88	97	495
-6	184	189	363
-5	397	377	156
-4	520	493	715
-3	439	471	753
-2	963	907	989
1	667	736	959
2	659	603	804
3	706	678	755
4	104	97	546
5	491	422	222
6	130	95	536
7	136	145	728
8	136	109	928
9	39	27	893
1,K,5			
-9	55	80	198
-6	239	313	586
-5	147	171	562
-4	251	281	11
-3	353	373	226
-2	465	524	509
1	235	261	669
2	272	273	406
3	632	577	83
4	344	339	680
5	248	252	584
6	278	246	856
7	111	121	718
8	104	109	356
1,K,9			
-8	55	66	648
-6	88	87	90
-5	211	227	766
-4	96	116	423
-3	304	385	453
-2	532	586	722
1	550	520	856
2	266	306	648
3	547	561	377
4	39	47	595
5	291	232	939
6	152	166	82
7	55	49	601
8	111	115	685
1,K,13			
-8	78	104	11
-7	55	80	727
-6	104	123	443
-5	55	69	326
-4	88	98	714
-3	333	361	857
-2	166	181	20
1	294	280	88
2	530	525	18
3	438	421	751
4	124	117	426
5	104	124	537
6	166	154	547
7	88	90	938
8	104	94	6
1,K,17			
-8	88	125	285
-7	39	76	92
-6	157	174	785
-5	157	205	586
-4	147	152	216
-3	166	177	101
-2	307	275	423
1	96	98	850
2	171	167	280
3	211	206	181
4	162	164	879
5	184	201	676
6	111	106	900
7	55	66	278
8	68	62	428
1,K,21			
-6	55	63	43
-5	68	89	25
-4	96	164	478
-2	211	214	982
1	68	88	854
2	141	154	868
3	283	297	466
4	141	120	897
5	167	[illegible]	5
6	55	57	256
7	68	71	535
1,K,25			
-6	39	60	382
-4	104	105	898
-3	78	68	110
-2	141	127	198
1	96	114	316
2	55	67	774
3	88	90	673
5	78	88	370
6	78	77	696
1,K,29			
-4	39	54	214
-3	68	63	163
-2	39	50	467
1	96	124	298
2	78	85	455
3	124	124	193
4	39	[illegible]	660
1,K,33			
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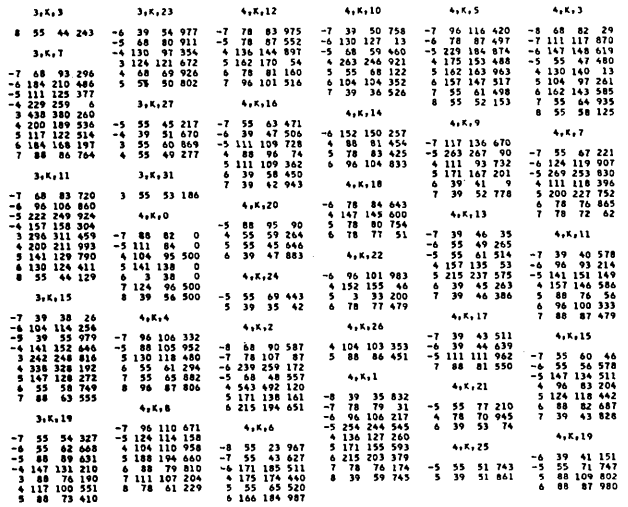
-2	68	67	948
1	55	36	146
1,K,3			
-9	55	83	907
-8	96	114	910
-7	141	166	166
-6	222	216	595
-5	304	284	631
-4	164	216	125
-3	463	475	191
-2	476	530	857
1	78	103	792
2	478	435	910
3	749	768	203
4	184	154	566
5	171	157	623
6	211	219	344
7	124	97	165
8	124	113	870
1,K,7			
-8	55	61	314
-7	39	60	814
-6	136	154	854
-5	248	281	3
-4	211	241	576
-3	324	343	423
-2	204	231	77
1	715	702	91
2	406	370	413
3	497	472	554
4	329	267	856
5	312	241	977
6	88	113	503
7	39	52	348
8	55	78	171
1,K,11			
-8	55	87	618
-7	55	64	6
-6	104	135	156
-5	162	201	330
-4	78	75	519
-3	429	424	783
-2	431	439	604
1	362	325	323
2	699	632	602
3	554	561	858
4	301	284	105
5	166	163	461
6	136	118	180
8	55	41	684
1,K,15			
-8	39	47	914
-7	78	114	378
-5	222	268	855
-4	157	195	391
-3	291	288	124
-2	399	431	926
1	157	179	740
2	171	206	26
3	301	289	164
4	96	112	351
5	68	77	787
6	39	49	472
7	55	55	342
8	130	114	990
1,K,19			
-7	39	47	736
-6	39	61	59
-5	130	159	10
-4	141	139	615
-3	239	266	548
-2	78	99	263
1	111	127	279
2	162	179	438
3	278	303	535
4	147	152	968
5	124	114	159
6	78	68	860
1,K,23			
-6	39	54	303
-5	78	107	400
-4	78	84	843
-3	78	86	899
-2	130	141	637
1	68	67	521
2	130	143	950
3	117	133	116
5	88	93	375
6	68	69	943
7	55	45	124
1,K,27			
-5	39	62	801
-4	55	39	280
-3	78	80	245
-2	111	119	976
1	88	105	13
2	136	128	68
3	104	118	260
4	55	64	736
1,K,31			
-3	55	68	522
-2	39	57	312
2	55	66	658
3	39	32	653
4	39	42	875
1,K,35			
2	55	49	734
2,K,0			
-8	55	55	0
-7	88	123	500
-5	147	166	500
-4	319	298	0
-3	471	470	0
2	266	212	500
3	573	428	500
4	104	51	500
5	104	89	500
6	211	148	500
7	147	106	0
8	78	73	0
2,K,4			
-7	104	154	840
-6	78	88	800
-5	88	104	848
-4	162	180	148
-3	117	127	340
2	530	488	424
3	211	211	886
4	96	90	136
5	184	129	19
6	147	114	875
8	147	146	393
2,K,8			
-8	55	90	684
-7	104	122	206
-6	55	43	167
-5	104	103	773
-4	175	188	363
-3	417	478	764
2	979	859	747
3	166	166	959
4	462	357	205
6	235	203	291
7	78	59	682
8	104	100	693
2,K,12			
-7	88	72	458
-6	78	68	584
-4	147	140	493
-3	204	207	51
2	275	265	73
3	130	144	634
4	78	82	849
6	248	214	523
7	104	73	0
8	78	52	48
2,K,16			
-7	78	92	912
-5	117	138	4
-4	111	111	928
-3	395	398	454
2	204	229	499
3	147	172	921
4	124	115	651
6	211	181	927
7	104	93	299
2,K,20			
-7	55	33	449
-6	55	59	185
-4	171	162	692
2	272	280	687
3	104	109	267
4	55	54	287
2,K,24			
-4	55	68	874
2	68	78	353
3	78	84	354
4	55	74	637
2,K,28			
-4	39	42	315
2	96	92	673
5	78	73	963
2,K,2			
-8	55	79	446
-6	88	117	798
-5	373	358	661
-4	370	403	237
-3	358	383	152
2	301	274	175
3	783	709	175
4	319	343	677
5	381	309	682
6	165	140	303
2,K,6			
-8	78	81	621
-7	88	108	601
-6	175	253	168
-5	307	285	40
-4	473	537	552
-3	427	494	406
2	649	555	626
3	731	663	520
4	104	93	974
5	325	262	94
6	130	111	524
7	211	195	692
2,K,10			
-6	188	233	416
-5	130	158	384
-4	473	434	868
-3	366	428	990
2	644	608	802
3	455	447	908
4	368	308	378
5	349	299	428
6	78	58	780
7	248	209	914
2,K,14			
-8	55	51	337
-6	117	138	758
-5	147	180	696
-4	171	185	271
-3	184	220	278
2	385	389	216
3	342	314	284
4	347	280	690
5	235	194	745
6	78	85	225
7	130	114	224
2,K,18			
-7	55	8	440
-6	78	102	147
-5	104	113	106
-4	269	265	591
-3	175	177	533
2	196	209	560
3	196	203	612
4	124	103	96
5	130	118	209
6	104	85	692
2,K,22			
-5	88	129	436
-4	104	116	989
-3	157	178	981
2	78	85	772
3	316	310	952
4	78	79	464
5	78	66	579
6	78	73	809
2,K,26			
-6	78	77	69
-5	78	72	790
-4	104	92	360
3	104	91	292
4	39	35	724
5	130	107	909
2,K,30			
-4	78	54	679
-3	55	25	856
2	68	60	530
4	39	46	992
2,K,1			
-8	78	85	150
-7	166	179	324
-6	117	156	656
-5	342	349	981
-4	307	324	993
-3	666	551	542
2	557	540	41
3	475	492	270
4	254	388	456
5	147	136	890
6	248	195	942
7	166	163	643
2,K,5			
-7	104	130	662
-6	104	143	813
-5	349	326	243
-4	304	339	364
-3	175	187	866
2	494	434	410
3	453	402	600
4	324	337	805
5	104	105	446
6	289	241	182
7	130	95	992
2,K,9			
-7	96	28	71
-6	55	65	99
-5	88	100	588
-4	286	294	576
-3	349	435	291
2	492	453	748
3	395	327	356
4	316	289	148
5	401	328	700
7	104	111	367
2,K,13			
-8	55	66	374
-5	242	266	83
-4	239	247	972
-3	188	213	525
2	307	314	212
3	130	138	428
4	254	220	449
5	166	140	44
6	147	111	177
2,K,17			
-6	55	74	951
-5	55	80	304
-4	269	220	416
-3	147	141	37
2	166	180	546
3	166	162	878
4	263	231	917
5	147	133	258
7	78	57	42
2,K,21			
-6	55	64	425
-5	104	144	768
-4	147	123	659
-3	78	81	412
2	147	178	861
3	211	192	140
6	78	59	790
7	78	61	381
2,K,25			
-6	78	57	626
-4	88	88	53
2	222	217	194
4	39	42	778
2,K,29			
-4	78	88	430
2	39	55	621
4	39	50	53
2,K,3			
-7	147	176	404
-6	175	214	336
-5	157	178	909
-4	175	213	2
-3	229	248	226
2	670	599	799
3	441	373	579
4	304	317	409
5	196	169	794
6	387	272	940
7	78	71	131
2,K,7			
-8	55	90	981
-6	55	74	467
-5	263	251	254
-4	272	251	411
-3	130	150	559
2	819	888	124
3	416	388	702
4	473	371	807
5	324	276	128
6	104	102	111
7	211	170	587
2,K,11			
-7	78	110	284
-5	362	354	634
-4	222	243	635
-3	395	379	99
2	204	170	998
3	3	48	128
4	338	363	129
5	248	216	624
6	78	82	752
7	196	149	944
2,K,15			
-8	55	53	752
-7	55	68	641
-6	55	86	517
-5	117	143	942
-4	196	195	828
-3	342	336	411
2	215	210	763
3	104	103	695
4	385	324	538
5	104	84	799
6	130	122	83
7	78	76	289
2,K,19			
-6	55	59	737
-5	104	111	321
-4	111	80	585
-3	184	185	772
2	147	153	349
3	3	58	351
4	184	163	850
5	184	172	211
6	147	136	421
7	104	92	600
2,K,23			
-5	78	62	819
-3	55	71	26
2	200	217	636
3	166	195	370
4	152	141	193
5	78	50	518
6	104	89	777
2,K,27			
-5	55	86	15
-4	39	47	104
2	68	79	881
3	78	72	616
4	68	77	501
2,K,31			
-4	39	29	609
3,K,0			
-8	55	45	500
-7	68	59	500
-5	211	178	0
-4	208	191	0
3	492	484	500
4	136	139	500
5	117	89	0
7	78	56	500
3,K,4			
-7	117	119	908
-6	157	138	264
-5	326	364	351
-4	235	263	345
3	453	414	856
4	441	375	891
5	421	411	368
6	211	172	528
7	55	68	852
3,K,8			
-7	104	105	232
-6	136	109	357
-5	219	236	721
-4	166	158	680
3	602	529	175
4	329	320	182
5	188	187	672
6	184	174	788
7	55	78	151
3,K,12			
-7	78	100	671
-6	104	116	479
-5	278	263	101
-4	88	85	75
3	130	130	603
4	427	402	636
5	211	184	18
6	104	109	107
8	55	30	732
3,K,16			
-7	78	101	1
-5	157	184	478
-4	208	237	432
3	196	219	925
4	147	138	855
5	141	140	470
3,K,20			
-7	39	37	346
-5	96	110	855
-4	78	86	665
3	141	143	249
4	222	219	334
5	141	129	809
6	55	52	871
7	55	44	288
3,K,24			
-6	78	86	89
-5	88	76	186
-4	39	41	32
3	147	140	599
5	88	88	75
6	55	56	338
3,K,28			
-5	55	56	638
3	78	74	985
4	55	47	88
5	78	59	504
3,K,2			
-8	111	129	702
-7	68	92	673
-6	136	128	93
-5	180	189	967
-4	331	308	104
3	88	85	645
4	141	110	86
5	344	96	646
6	157	114	67
7	117	150	224
3,K,6			
-8	78	76	13
-7	55	31	974
-6	78	92	630
-5	117	131	27
-4	235	202	489
3	196	194	312
4	366	113	122
6	204	175	589
7	147	133	525
8	88	73	940
3,K,10			
-8	130	114	372
-7	39	39	65
-6	68	84	834
-5	96	100	254
-4	96	95	85
3	229	197	404
6	78	84	758
7	88	88	904
8	104	78	355
3,K,14			
-6	135	139	222
-5	55	61	90
-4	124	106	501
3	68	86	756
4	96	93	605
5	147	148	52
6	88	91	162
7	104	90	282
3,K,18			
-6	96	112	444
-5	55	64	815
-4	78	79	632
3	68	72	874
5	88	90	27
7	55	46	623
3,K,22			
-5	39	52	528
-4	124	124	919
3	55	70	768
5	55	48	443
6	55	56	900
3,K,26			
-4	55	42	480
5	104	37	981
3,K,1			
-7	55	57	26
-6	235	234	684
-4	235	240	176
3	266	286	219
4	278	249	747
5	333	300	832
6	307	278	108
7	104	82	281
8	88	80	434
3,K,5			
-8	68	78	864
-7	68	69	248
-6	39	92	80
-5	171	171	946
-4	291	340	591
3	283	266	582
4	299	290	49
5	342	326	73
6	130	109	465
7	88	91	625
8	55	45	975
3,K,9			
-8	39	48	39
-7	68	82	642
-6	192	184	464
-4	130	125	47
3	269	296	763
4	215	209	364
5	219	202	569
6	55	76	865
7	88	74	50
3,K,13			
-7	68	73	963
-6	55	82	701
-4	377	370	283
3	147	159	128
4	254	201	636
5	130	133	756
6	130	134	173
7	88	88	485
3,K,17			
-6	96	115	160
-5	39	50	871
-4	171	163	664
3	141	158	666
4	68	54	213
5	147	147	271
6	104	102	522
7	104	77	767
3,K,21			
-6	55	69	535
-4	141	143	941
3	88	91	302
4	78	82	406
5	117	118	584
6	88	75	925
3,K,25			
-4	39	64	355
3	104	124	415
5	78	62	916
6	78	57	265
3,K,29			
-4	39	44	730
3,K,3			
-6	180	188	144
-5	184	192	153
-4	478	447	640
3	251	246	606
4	269	231	273
5	229	223	966
6	117	119	621
7	117	125	504

Table 4 (*cont.*)



and if

$$\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0} \qquad (1)$$

$E_{\mathbf{h}_1}$, $E_{\mathbf{h}_2}$, and $E_{\mathbf{h}_3}$ are all large,

then the probability of

$$\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}=2\pi n \qquad (2)$$

is high. $\varphi_{\mathbf{h}}$ is the phase of the structure factor $E_{\mathbf{h}}$.

This equation (2) corresponds to the equation

$$S_{\mathbf{h}_1}\times S_{\mathbf{h}_2}\times S_{\mathbf{h}_3}\approx +1 \qquad (3)$$

for the centrosymmetric case. $S_{\mathbf{h}}$ is the sign of the structure factor $E_{\mathbf{h}}$.

It was decided to try to solve the structure using equation (2). As initial phases the following were chosen:

h	k	l	E	φ
1	4	0	2·27	0°
4	6	1	1·70	60°

The choice of parity groups for the initial phases has been discussed by Hauptman & Karle (1956). The choice of 140 and 461 was made since these two sets of indices could be combined by (2) with indices of large values of E. The phase of 461 was chosen equal to 60° to specify the enantiomorph.

Table 5. *Comparison between bond lengths in β- and α_1-bromopicrotoxinin*

Standard deviations in both investigations: C–Br 0·015 Å, C–O 0·019–0·025 Å, C–C 0·021–0·027 Å.

Bond type		β-Bromopicrotoxinin (this investigation)	α_1-Bromopicrotoxinin [from Craven's (1962) data]
Br–C(sp^3)	Br —C	$1{\cdot}99_6$ Å	$1{\cdot}97_8$ Å
O–C(sp^3) in 5-membered ring	O(1)—C(6)	$1{\cdot}45_2$	$1{\cdot}40_9$
	O(1)—C(8)	$1{\cdot}47_2$	$1{\cdot}48_7$
	O(4)—C(2)	$1{\cdot}47_0$	$1{\cdot}44_1$
	O(6)—C(3)	$1{\cdot}48_8$	$1{\cdot}44_1$
O–C and O=C in 5-membered lactone ring	O(4)—C(14)	$1{\cdot}34_7$	$1{\cdot}37_3$
	O(3)=C(14)	$1{\cdot}21_1$	$1{\cdot}20_7$
	O(6)—C(15)	$1{\cdot}32_3$	$1{\cdot}36_3$
	O(5)=C(15)	$1{\cdot}24_1$	$1{\cdot}24_5$
C–O and C–C in 3-membered ring	O(2)—C(12)	$1{\cdot}38_2$	$1{\cdot}45_6$
	O(2)—C(13)	$1{\cdot}39_9$	$1{\cdot}41_0$
	C(12)—C(13)	$1{\cdot}43_0$	$1{\cdot}49_7$
C(sp^2)–C(epoxide)	C(13)–C(14)	$1{\cdot}50_4$	$1{\cdot}49_8$
C(sp^3)–C(epoxide)	C(1)—C(13)	$1{\cdot}51_4$	$1{\cdot}49_6$
	C(11)–C(12)	$1{\cdot}53_9$	$1{\cdot}54_6$
C(sp^3)–C(sp^2)	C(5)—C(15)	$1{\cdot}49_2$	$1{\cdot}48_3$
C(sp^3)–C(sp^3)	C(1)—C(2)	$1{\cdot}54_0$	$1{\cdot}56_0$
	C(1)—C(6)	$1{\cdot}55_1$	$1{\cdot}54_6$
	C(1)—C(7)	$1{\cdot}50_3$	$1{\cdot}48_9$
	C(2)—C(3)	$1{\cdot}54_1$	$1{\cdot}49_6$
	C(3)—C(4)	$1{\cdot}52_1$	$1{\cdot}56_8$
	C(4)—C(5)	$1{\cdot}50_7$	$1{\cdot}53_4$
	C(4)—C(8)	$1{\cdot}57_6$	$1{\cdot}53_2$
	C(5)—C(6)	$1{\cdot}54_8$	$1{\cdot}55_2$
	C(6)—C(11)	$1{\cdot}56_7$	$1{\cdot}53_7$
	C(8)—C(9)	$1{\cdot}50_6$	$1{\cdot}49_6$
	C(8)—C(10)	$1{\cdot}52_5$	$1{\cdot}54_1$
	average	$1{\cdot}53_5$	$1{\cdot}53_2$

Forty phases were generated from these first phases, a new phase was included only if it had the same value indicated by more than one relation (2).

These 40 phases were now combined to give 450 phases; a new phase was included if it had a value indicated by one or the same value by several relations. Another 60 phases had indications of different values. These 60 phases were estimated by the weighted mean:

$$\varphi_h = \frac{\sum_i (E^i_{h_1} E^i_{h_2})\ \varphi_i}{\sum_i E^i_{h_1} E^i_{h_2}} .$$

φ_i is the phase found by the relation

$$\varphi_i + \varphi^i_{h_1} + \varphi^i_{h_2} = 0 .$$

When the refinement was finished the values of the phases were compared, and the following average deviations were found.

	Average deviation from refined structure
All 510 phases	40°
The first 40 phases	21
The last 60 phases	40

Table 6. *Comparison between valency angles in β- and α_1-bromopicrotoxinin*

Standard deviations are given for the β compound.
In the determination of the α_1 compound standard deviations ranging from 1·1° to 1·7° were found.

Angle	β-Bromopicrotoxinin (this investigation)		α_1-Bromopicrotoxinin [from Craven's (1962) data]
C(6)—O(1)—C(8)	1·2°	107·0°	107·0°
C(12)–O(2)—C(13)	1·3	61·9	63·0
C(2)—O(4)—C(14)	1·3	111·3	111·9
C(3)—O(6)—C(15)	1·3	106·0	106·4
C(2)—C(1)—C(6)	1·2	114·6	114·8
C(2)– –C(7)	1·3	112·6	112·7
C(2)– –C(13)	1·2	102·5	102·4
C(6)– –C(7)	1·3	114·3	113·4
C(6)– –C(13)	1·2	99·9	101·8
C(7)– –C(13)	1·4	111·6	110·5
O(4)—C(2)—C(1)	1·1	106·4	106·6
O(4)– –C(3)	1·2	109·1	109·1
C(1)– –C(3)	1·2	113·5	114·3
O(6)—C(3)—C(2)	1·3	106·1	108·7
O(6)– –C(4)	1·2	102·1	102·7
C(2)– –C(4)	1·3	116·3	114·1
C(3)—C(4)—C(5)	1·2	97·5	96·9
C(3)– –C(8)	1·3	125·5	124·4
C(5)– –C(8)	1·3	99·7	102·5
C(4)—C(5)—C(6)	1·2	99·4	96·8
C(4)– –C(15)	1·3	102·4	102·4
C(6)– –C(15)	1·4	117·2	118·4
O(1)—C(6)—C(1)	1·2	109·9	111·5
O(1)– –C(5)	1·3	100·2	99·9
O(1)– –C(11)	1·3	115·8	115·0
C(1)– –C(5)	1·2	115·6	115·3
C(1)– –C(11)	1·3	104·1	104·0
C(5)– –C(11)	1·3	111·8	111·6
O(1)—C(8)—C(4)	1·3	105·4	103·8
O(1)– –C(9)	1·3	107·7	108·2
O(1)– –C(10)	1·4	110·8	111·8
C(4)– –C(9)	1·4	108·9	115·3
C(4)– –C(10)	1·3	109·2	114·2
C(9)– –C(10)	1·6	114·5	103·6
C(8)—C——Br	1·0	110·4	115·7
C(6)—C(11)–C(12)	1·5	99·9	102·2
O(2)—C(12)–C(11)	1·6	117·2	111·9
O(2)– –C(13)	1·3	59·6	57·0
C(11)– –C(13)	1·6	108·1	104·8
O(2)—C(13)–C(1)	1·6	119·7	118·6
O(2)– –C(12)	1·3	58·5	60·0
O(2)– –C(14)	1·6	119·0	120·7
C(1)– –C(12)	1·6	111·3	110·9
C(1)– –C(14)	1·5	107·4	108·6
C(12)– –C(14)	1·7	134·3	131·3
O(3)=C(14)–O(4)	1·8	121·2	121·3
O(3)= –C(13)	1·8	129·5	130·3
O(4)– –C(13)	1·6	109·3	108·1
C(5)=C(15)–O(6)	1·9	120·0	119·2
C(5)= –C(5)	1·8	129·1	129·8
O(6)– –C(5)	1·4	110·8	111·0

A Fourier synthesis was calculated from the 510 phases.

From the Fourier map the position of the bromine atom was found. Light atoms were placed on 21 of the next highest peaks; 9 of these positions were later shown to be wrong. The 21 positions were chosen without chemical considerations to ensure the objectivity of the method. The structure coud probably just as well have been solved from a three-dimensional Patterson synthesis.

Successive diagonal least-squares and Fourier calculations gave the positions of the 15 carbon atoms and the 6 oxygen atoms and an R value (observed reflexions only) of 0·17. The computations described so far were performed on the computer GIER. The Fourier program was a machine order program written by Lauesen (1964). The other computations were carried out using Algol programs written by Danielsen.*

Anisotropic refinement by the program written by Gantzel, Sparks, Long & Trueblood (1967) was performed on the IBM 7090 computer at the NEUCC installation in Copenhagen. This reduced the R value to 0·11. In Table 2 the final geometric coordinates are shown, in Table 3 the final anisotropic temperature factors, and in Table 4 the observed and calculated $|F|$ values.

Description and discussion of the structure

The structure determination showed that β-bromopicrotoxinin and the α_1 isomer described by Craven (1962) are epimeric compounds. The difference between their configurations consists in the interchange of a CH_3 group and a CH_2Br group at the asymmetric centre C(8). This result agrees with the conclusions drawn by Carman (1963) from a nuclear magnetic resonance study.

Comparisons between the two isomers are made in Fig. 1 and Tables 5, 6 and 7. The numbers given to the atoms are in accordance with the ones used by Craven (1962); note, however, that C(9) and C(10) are interchanged relative to Carman's notation. It is seen that in β-bromopicrotoxinin the bromine atom is attached to C(10), and C(9) is a methyl carbon, whereas the α_1 isomer has the bromine atom bonded to C(9), and C(10) is the methyl carbon. Fig. 1 shows the absolute configuration of the β-bromopicrotoxinin molecule. This has been assigned by comparison with the α_1 isomer for which the absolute configuration is known, and which must be sterically very closely related to the β isomer as inferred *e.g.* from the way the two compounds are synthesized. The knowledge of the absolute configuration of β-bromopicrotoxinin made it possible to assign the correct space group to the crystals, and $P4_3$ had to be chosen instead of $P4_1$ in order to obtain consistent configurations of the isomers.

* D50, Program system for direct methods; D28, diagonal least-squares program; D45, stepwise minimization of the R value. Kemisk Institut, Aarhus Universitet.

Table 7. *Comparison between some intramolecular non-bonded distances in β- and α_1-bromopicrotoxinin*

	β-Bromopicrotoxinin (this investigation)	α_1-Bromopicrotoxinin (Craven, 1962)
Br——C(4)	—	3·30 Å
–C(9)	3·30 Å	—
–C(8)	2·90	2·98
–O(1)	3·24	3·41
C(2)—C(10)	3·25	3·18
C(7)—C(10)	3·56	3·36
–O(1)	2·85	2·86
–O(2)	2·86	2·77
C(15)–C(12)	3·15	3·18
–C(13)	3·03	3·11
–C(14)	3·26	3·34
O(5)—C(12)	3·29	3·29
–C(13)	3·51	3·56
–C(14)	3·66	3·70
–O(3)	4·07	4·29

The crystal structure determinations of both isomers appear to be of approximately the same accuracy as judged from the standard deviations given on bond lengths and valency angles which were calculated on the BONDLA program in the Crystal Structure Calculation System X-ray-63, from the University of Maryland, Computer Science Center.

In Table 5 are registered 27 pairs of equivalent bond lengths found in the two isomers. The difference between two equivalent bonds is in 14 cases less than the standard deviation (σ) of the bond length in question as found in this investigation, in 8 cases less than 2σ and in the remaining 5 cases less than 3σ. All these differences may thus be considered insignificant. It is noticed that two of the largest discrepancies are found in the three-membered rings.

In Table 6, 51 pairs of chemically equivalent valency angles are recorded. In 33 cases the difference between two equivalent valency angles is less than σ (the standard deviation of the corresponding angle as found in this investigation), in 9 cases less than 2σ, in 4 cases less than 3σ, in 2 cases less than 4σ and in the last three cases differences close to 5σ, 6σ and 8σ respectively are seen. These differences may be considered insignificant apart from the last named, in all of which the epimeric centre C(8) is involved, which will be discussed separately. Table 6 shows that rather big deviations from ideal valency angles are found in several cases as a consequence of the strain imposed by the fusion of several rings to form the complex skeleton of the bromopicrotoxinins. The most irregular arrangement of bonds is found at C(13). This is quite natural, since this carbon atom takes part in the formation of three rings, one three-membered and two five-membered. Another atom at which considerable strain is concentrated is C(4), as indicated primarily by large deviations of the three angles C–C(4)–C from 109·5°, but several angles C–C–C(4) are also appreciably affected.

In Table 7 comparison is made between some equivalent non-bonded interatomic distances in the two

epimers. In most cases only small deviations, less than 0·1 Å are found; these are however in a number of cases definitely significant. The different configuration of the two molecules must to some extent influence the surroundings of the atoms C(9), C(10) and Br, and actually deviations of about 0·2 Å between the distances C(7)–C(10) and between the distances Br–O(1) are found. A similar deviation between the distances O(5)–O(3) indicates that the relative positions of the two carbonyl groups C(15)=O(5) and C(14)=O(3) are slightly different in the two compounds. This may probably be attributed to the packing of the molecules.

The molecular geometries of the main part of the two isomers therefore match very closely. The angular

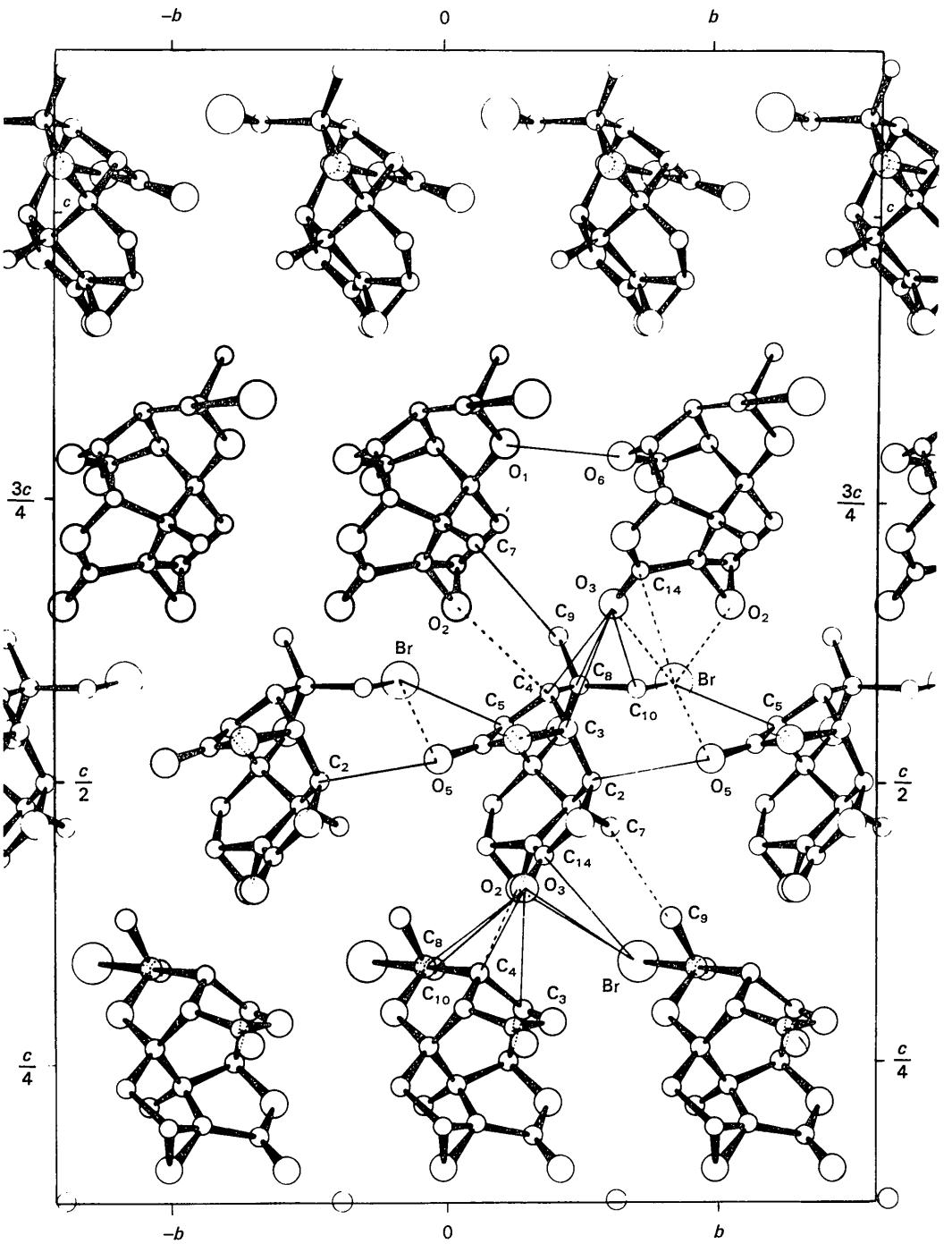


Fig. 2. The structure viewed along the *a* axis. Full lines and broken lines are used to distinguish between distances from the central molecule to neighbour molecules with common *b* and *c* coordinates but placed at different *a* levels (*cf.* Table 8).

Table 8. *Intermolecular distances*

The table comprises distances smaller than 3·6 Å involving only carbon and oxygen atoms and distances smaller than 4·0 Å involving the bromine atom.

I	x , y , z			V	y , $\bar{x}+2$, $z+\frac{1}{4}$		
II	$x-1$, y , z			VI	$y+1$, $\bar{x}+2$, $z+\frac{1}{4}$		
III	x , $y+1$, z			VII	$y+1$, $\bar{x}+1$, $z+\frac{1}{4}$		
IV	$x-1$, $y+1$, z			VIII	y , $\bar{x}+1$, $z+\frac{1}{4}$		
O(1)I	O(6)II	3·28 Å		C(9)I	C(7)VIII	3·58 Å	
C(2)I	O(5)III	3·21					
C(3)I	O(3)VI	3·33		BrI	C(5)III	3·90 Å	
C(4)I	O(3)VI	3·04		BrI	O(5)IV	3·84	
C(8)I	O(3)VI	3·47		BrI	O(2)V	3·87	
C(10)I	O(3)VI	3·25		BrI	O(3)V	3·80	
C(4)I	O(2)VII	3·49		BrI	C(14)V	3·76	

distribution at the epimeric centre, however, is significantly different in the two compounds. It is remarkable that the arrangement in β-bromopicrotoxinin is much more regular. In accordance with this it is evident from molecular models that the steric strain in this compound must be much smaller than in the α_1 isomer. A model of that compound suggests that the angles C(8)–C(9)–Br and C(4)–C(8)–C(9) should be expanded whereas the angle C(9)–C(8)–C(10) should be smaller than in regular tetrahedral arrangements; and significant deviations of these angles from 109·5° in the indicated directions are actually found. From such simple steric considerations it is not possible to explain why two more angles show deviations that are probably significant from 109·5°, *i.e.* in the α_1 isomer C(4)–C(8)–C(10) and in the β isomer C(9)–C(8)–C(10).

Further model considerations show that the conformation adopted by the CH_2Br group in the β isomer is undoubtedly the most favourable, but that this is apparently not the case with the α_1 isomer. In this compound it appears that a conformation with the bromine atom in a *trans* position relative to C(4) might give rise to less angular strain than the conformation found. One may expect that this conformation is present in the crystals of α_2-bromopicrotoxinin; this is generally considered to be a polymorph of α_1-bromopicrotoxinin, but the structure has not been determined.

The molecular packing is shown in Fig. 2. The roughly spherical molecule is surrounded by 14 neighbouring molecules, 6 at the same c level, 4 at each of the adjacent c levels. The shortest intermolecular contacts are listed in Table 8. The bromine atom approaches five carbon and oxygen atoms at distances 3·76–3·90 Å. In the crystal structure of the α_1 isomer similar distances were found (3·88–3·99 Å) but in that structure furthermore one very much shorter contact [3·37 Å between Br and O(2)] was observed. Craven suggested that this might possibly be interpreted as a very weak intermolecular bonding interaction, but the present structure determination does not support this view. No particular short contacts between carbon and oxygen atoms are noticed. One distance [C(4)–O(3), 3·04 Å] is appreciably shorter than the other, but this has no similar short counterpart in the crystal structure of the α_1 isomer. Thus it appears that in both β- and α_1-bromopicrotoxinin the intermolecular contacts are exclusively of the van der Waals' type.

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