The Crystal Structure of Retusamine, α'-Bromo-D-camphor-*trans*-π-sulphonate Monohydrate
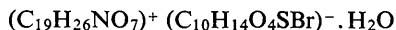
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The structure of the *Crotalaria* alkaloid, retusamine, has been determined as its monohydrated bromo-camphorsulphonate salt. The crystals are triclinic, space group $P1$, with one formula unit

$$(C_{19}H_{26}NO_7)^+ \ (C_{10}H_{14}O_4SBr)^- . H_2O$$

in the unit cell of dimensions $a=15\cdot10, b=7\cdot12, c=7\cdot32$ Å; $\alpha=91\cdot3, \beta=93\cdot2, \gamma=96\cdot9°$ taken at $-120°$ C. The analysis was based on 3287 reflexions, 3124 of which were observed. From an initial electron density map with all phases equal to zero, the anion was located and two further maps were required to solve the complete structure which was then refined by full-matrix least-squares methods to a final R of $0\cdot152$. The absolute configurations of both cation and anion were determined from this structure by Bijvoet's method and are shown below, numbered according to accepted chemical conventions.
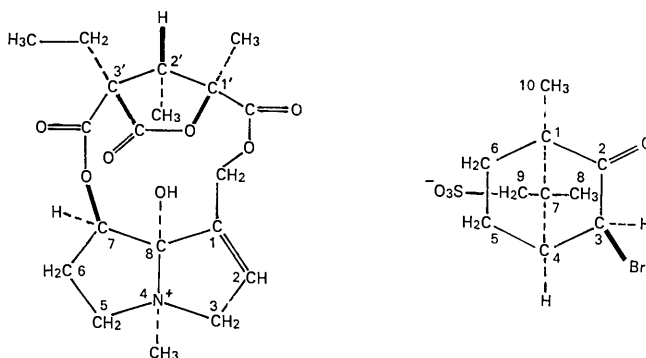
The water molecule forms a hydrogen-bond network linking the OH group of the retusamine cation to two of the sulphonate oxygen atoms. Of particular interest is the very long ring-fusion C–N bond (1·64 Å), since it is readily cleaved on regeneration of the free base to give an 8-membered cyclic amino-ketone exhibiting transannular interaction between the trigonal nitrogen atom and the carbonyl group. Also of general stereochemical interest are the observations that in the anion, the bromine atom is in the *endo* position and the sulphonate group is attached to C-9, that is *trans*-π to the keto group.

Introduction

The legume *Crotalaria retusa L.* which grows in the Kimberley area of northern Australia is known to contain alkaloids which cause liver damage in stock. The major alkaloids were shown (Culvenor & Smith, 1957) to be monocrotaline and another pyrrolizidine alkaloid named retusine, the structure of which was determined by chemical and spectroscopic methods. These workers also isolated a very small quantity of a water soluble base which they called retusamine. This alkaloid analysed for $C_{19}H_{25}NO_7$ or $C_{20}H_{27}NO_7$ and appeared to have chemical properties similar to those of otosenine (Zhdanovich & Men'shiokv, 1941), a cyclic diester of a known acid and an amino-alcohol of unknown constitution.

Because of the small quantity of retusamine available, it was decided to determine its structure by single-crystal X-ray diffraction methods.

A number of 'heavy atom' derivatives were prepared and their crystallographic properties were examined

and reported briefly (Wunderlich, 1967). The 3-bromo-D-camphor-*trans*-π-sulphonate was chosen for the complete structure determination because the crystal contains only one 'molecule' in the acentric triclinic unit cell, ensuring a straightforward analysis. Furthermore it would provide an opportunity to study the stereochemistry of this derivative of camphor and to provide confirmation of the absolute configuration of camphor as determined by chemical methods (Fredga & Miettinen, 1947).

Experimental

Prismatic needles were obtained by adding an equivalent of α'-bromo-D-camphor-*trans*-π-sulphonic acid to an aqueous solution of retusamine and recrystallizing the product from water.

The unit-cell dimensions were measured at $-120°C$ from Weissenberg and precession photographs of crystals mounted about the b and c axes using Cu $K\alpha$ radiation. The powder pattern of highly purified silicon was used as an internal standard on all the films.

The density was not determined owing to the scarcity of crystals, but the density calculated for one 'molecule' in the unit cell is what would be expected for the material.

Crystal data

Retusamine α'-bromo-D-camphor-*trans*-π-sulphonate monohydrate, $C_{29}H_{42}O_{12}NSBr$, M.W. 708·6.

Triclinic

$a = 15·10 \pm 5$, $b = 7·12 \pm 2$, $c = 7·32 \pm 2$ Å
$\alpha = 91·3 \pm 0·1$, $\beta = 93·2 \pm 0·2$, $\gamma = 96·9 \pm 0·2°$
$V = 779 \pm 4$ Å^3, D_m not measured, $Z = 1$, $D_x = 1·511$ g.cm^{-3},
$F(000) = 370$, $\mu = 32$ cm^{-1} for Cu $K\alpha$ radiation.

Since both the alkaloid and the camphorsulphonic acid are optically active, the space group must be $P1$.

The intensities of 3287 reflexions were recorded on film by the Weissenberg method and measured by visual comparison with a standard scale. Of these 3124 (95%) were observed. Corrections for the Lorentz and polarization factors were computed but no account was taken of absorption or extinction.

Structure determination

As the space group is $P1$, the origin of the unit cell is not fixed and was chosen at the bromine atom.

A three-dimensional electron density map with all phase angles equal to zero was computed and, as had been expected, it was possible to identify the bromo-camphorsulphonate ion as well as some fragments of the retusamine cation. Once one of two centrosymmetrically related peaks was assigned to C(23) (that is, the atom to which the bromine atom is bonded; for numbering see Fig.1) all other 'real' atom sites and their symmetry 'ghosts' were easily differentiated. Van der Waals contact distances were used as criteria to identify 'real' atom sites in the retusamine molecule. The configuration of the sulphonate group was *trans* with respect to the keto group, in contradiction of the structure generally accepted (Simonsen, 1949) for this widely used resolving agent. At this stage then, only the non-hydrogen atoms of the bromocamphorsulphonate ion were used to calculate phases for the second electron density distribution. The discrepancy index $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ was 0·27 for all 3287 observed and unobserved reflexions.

The 'ghosts' in this map were now much attenuated and it was possible to recognize one five-membered ring containing a double bond, the γ-lactone ring and two planar ester groups as well as an ethyl and two methyl groups.

A strong isolated peak distant about 2·7–2·8 Å from two sulphonate oxygen atoms was interpreted as due to a water molecule of crystallization. This had not been anticipated since neither micro-analysis nor den-

sity measurement had been carried out at this time because of the scarcity of material.

A third electron density map was computed with phases obtained by including the bromocamphorsulphonate ion, 22 atoms of the retusamine cation and the water molecule in the calculation of structure factors for which R decreased to 0·24.

The 'ghost' peaks had now almost totally disappeared and the remaining 5 atoms were readily found and identified to reveal the total molecular structure of the retusamine cation. A cycle of full-matrix least-squares refinement (Busing & Levy, 1959) was carried out in which only the scale and temperature factors were varied. The R value fell to 0·23. A second cycle in which all positional parameters were varied resulted in considerable shifts (up to 0·1 Å for some atoms) but R remained substantially the same, being now 0·227. Inspection of observed and calculated structure factors indicated that individual scale factors should be given to each hkl level. In all, 10 scale factors were used, each being estimated as $(\Sigma F_o^2/\Sigma F_c^2)^{\frac{1}{2}}$ for the appropriate group of reflexions. The structure factors calculated with these scale factors resulted in a discrepancy factor of 0·168.

Two further cycles of least-squares refinement were run, varying 160* scale, positional and temperature parameters. Again, although R fell by only 0·01 to 0·158, inspection of $\Sigma w(F_o^2 - F_c^2)^2$ and the bond lengths after each cycle clearly indicated that the structure was refining satisfactorily and now most bonds did not differ significantly from normal values (Sutton, 1958). The ring fusion C–N bond did however exceed the distance generally found in alkaloids (Hamilton, Hamor, Robertson & Sim, 1962) by as many as six standard deviations and several C–C bonds deviated also by two to three standard deviations. Because of the interest in this novel pyrrolizidine system it was decided to compute one final least-squares cycle of refinement. For this cycle only observed reflexions were used in setting up the normal equations while unobserved reflexions were included in the calculation of R which had fallen to 0·151. An analysis of R is made in Table 1.

The correlation matrix whose elements are $a_{ij}/(a_{ii} \times a_{jj})^{\frac{1}{2}}$ was calculated to determine if some indeterminate

Table 1. *Values of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ for different classes of reflexion*

	R	Range of sin θ	R	Number of reflexions
All planes	0·152	0·00–0·40	0·125	230
All $0kl$	0·166	0·40–0·52	0·126	263
All $h0l$	0·134	0·52–0·61	0·137	312
All $hk0$	0·126	0·61–0·65	0·147	169
		0·65–0·70	0·131	255
		0·70–0·75	0·165	265
		0·75–0·80	0·177	323
		0·80–0·85	0·165	317
		0·90–0·99	0·224	690

* The maximum number of variables which could be varied simultaneously using the program of Busing & Levy (1959) for the IBM 704 computer.

parameters were not responsible for the abnormally long C–N ring fusion bond. No such evidence was found, the largest elements of the correlation matrix being about 0·25, representing interaction between scale factors, and the highest elements relation C(7) and N being 0·03 between positional parameters and 0·06 between thermal parameters. A three-dimensional difference synthesis computed before the final least-squares cycle of refinement contained many maxima, some of which could be assigned to hydrogen atom sites, others to indications of shifts in positional parameters or of anisotropic thermal vibrations of the Br atom, while others could not be given a physical interpretation and were assumed to have arisen from random and systematic experimental errors. These results were not encouraging and no further difference synthesis was calculated. However, since the highest electron density found in this difference map was 1·6 e.Å^{-3}, located at the Br atom site, it did serve to show that only one water molecule of crystallization was present in the crystal. The final atomic positional and isotropic temperature factors are listed in Table 2.

The mean standard deviations calculated from the final full-matrix least-squares computation are:

$$\sigma_x = \sigma_y = \sigma_z = 0\cdot003 \text{ Å}, \quad \sigma_B = 0\cdot06 \text{ Å}^2 \text{ for S,}$$
$$\sigma_x = 0\cdot011 \text{ Å}, \quad \sigma_y = \sigma_z = 0\cdot014 \text{ Å}, \quad \sigma_B = 0\cdot20 \text{ Å}^2 \text{ for O,}$$
$$\sigma_x = 0\cdot15 \text{ Å}, \quad \sigma_y = \sigma_z = 0\cdot018 \text{ Å}, \quad \sigma_B = 0\cdot25 \text{ Å}^2 \text{ for C, and}$$
$$\sigma_B = 0\cdot04 \text{ Å}^2 \text{ for Br.}$$

The atomic scattering curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for C, N, O, that of Dawson (1960) for S. The Br curve of Thomas & Umeda (1957) was corrected for anomalous scattering, using the data of Dauben & Templeton (1955).

The observed values of the structure factors are listed in Table 3.

Absolute configuration

The method of Bijvoet, Peerdeman & van Bommel (1951) was used to determine the absolute configuration. The anomalous scattering of Cu $K\alpha$ X-radiation by Br has been shown (Peterson, 1955; Peerdeman, 1956) to be large enough to be generally observable by photographic methods and in our case too it was possible to distinguish differences between certain $h0l$ and $h0\bar{l}$ reflexions. The Weissenberg goniometer of Mathieson (1951) was modified so that the crystal could be rotated by a little over 360° for this triclinic case. Reflexions, the intensities of which were the most sensitive to the anomalous scattering effect were those for which A, the real component of F, was much smaller than the imaginary part B and these were all weak. A selection was readily made and the results are listed in Table 4.

The absolute configuration for both molecules is correctly indicated by the atomic parameters given in Table 2 and a right-handed set of axes.

It may be seen from the perspective representations on Fig. 1 that the absolute configuration of the bromocamphorsulphonate anion is the same as that determined chemically by Fredga & Miettinen (1947) for camphor and that the alkaloid moiety has the same absolute configuration as that found for jacobine, a related pyrrolizidine alkaloid (Fridrichsons, Mathieson & Sutor, 1963).

Discussion of the structure

The quaternary ammonium salt nature of this derivative of retusamine is clearly demonstrated both by the infrared spectra, which show the disappearance of the

Table 2. *Atomic positional and temperature parameters*

	x	y	z	B
Retusamine cation				
C(1)	0·704	0·036	0·859	3·70 Å²
C(2)	0·759	0·075	0·006	3·58
C(3)	0·753	0·934	0·148	4·55
C(4)	0·626	0·671	0·157	5·35
C(5)	0·553	0·793	0·114	4·12
C(6)	0·555	0·813	0·911	3·04
C(7)	0·655	0·842	0·862	3·10
C(8)	0·700	0·154	0·698	3·97
C(9)	0·763	0·619	0·997	4·59
C(10)	0·423	0·934	0·816	3·16
C(11)	0·381	0·106	0·763	3·29
C(12)	0·280	0·079	0·802	4·43
C(13)	0·233	0·253	0·772	5·75
C(14)	0·401	0·170	0·570	3·34
C(15)	0·408	0·006	0·430	4·38
C(16)	0·481	0·324	0·591	3·51
C(17)	0·465	0·495	0·471	4·61
C(18)	0·571	0·272	0·560	3·67
C(19)	0·429	0·278	0·881	3·49
O(1)	0·662	0·727	0·710	3·32
O(2)	0·511	0·969	0·849	3·24
O(3)	0·380	0·774	0·828	4·81
O(4)	0·422	0·307	0·044	4·68
O(5)	0·480	0·392	0·780	3·65
O(6)	0·590	0·227	0·401	5·68
O(7)	0·622	0·252	0·708	3·53
N	0·702	0·759	0·045	3·30
Bromocamporsulphonate anion				
C(20)	0·223	0·582	0·338	4·86
C(21)	0·132	0·634	0·267	4·04
C(22)	0·132	0·846	0·237	3·86
C(23)	0·032	0·875	0·230	3·39
C(24)	0·984	0·675	0·246	3·85
C(25)	0·995	0·559	0·064	2·65
C(26)	0·099	0·542	0·084	4·21
C(27)	0·049	0·602	0·393	3·56
C(28)	0·068	0·719	0·574	4·16
C(29)	0·030	0·396	0·429	3·69
O(8)	0·194	0·967	0·226	5·08
O(9)	0·922	0·129	0·559	5·49
O(10)	0·895	0·450	0·638	3·91
O(11)	0·856	0·318	0·330	4·37
S	0·916	0·316	0·493	3·45
Br	0	0	0	4·38
Water of crystallization				
O(12)	0·816	0·780	0·556	4·22

Table 3. *List of observed and calculated structure factors*

Unobserved reflexions are starred.

H	L	10F_o	10F_c
K = 0			
1	0	315	277
2	0	509	676
3	0	274	334
4	0	338	359
5	0	291	342
6	0	136	132
7	0	151	173
8	0	222	247
9	0	165	175
10	0	228	235
11	0	128	151
12	0	155	151
13	0	122	118
14	0	166	154
15	0	33	27
16	0	49	54
17	0	42	38
18	0	42	28
19	0	33	14
0	1	221	269
1	1	531	678
-1	1	491	609
2	1	375	342
-2	1	314	382
3	1	385	433
-3	1	565	631
4	1	329	336
-4	1	563	727
5	1	396	445
-5	1	422	406
6	1	312	300
-6	1	281	317
7	1	194	226
-7	1	526	572
8	1	359	369
-8	1	163	198
9	1	287	326
-9	1	343	354
10	1	114	99
-10	1	125	147
11	1	134	128
-11	1	116	122
12	1	49	52
-12	1	131	155
13	1	70	80
-13	1	48	55
14	1	102	114
-14	1	44	61
15	1	71	68
-15	1	9*	13
16	1	113	100
-16	1	87	89
17	1	67	76
-17	1	48	46
18	1	84	74
-18	1	72	66
19	1	37	44
-19	1	18	17
0	2	252	236
1	2	533	592
-1	2	482	510
2	2	440	498
-2	2	549	592
3	2	207	236
-3	2	217	178
4	2	272	310
-4	2	311	301
5	2	301	306
-5	2	100	112
6	2	79	45
-6	2	211	201
7	2	122	125
-7	2	217	246
8	2	53	58
-8	2	101	97
9	2	200	202
-9	2	162	168
10	2	175	184
-10	2	141	143
11	2	181	192
-11	2	177	172
12	2	218	239
-12	2	166	168
13	2	88	99
-13	2	143	140
14	2	160	123
-14	2	9*	30
15	2	28	5
-15	2	94	84
16	2	16	20
-16	2	67	52
17	2	64	54
-17	2	63	61
18	2	15	[illegible]
-18	2	6*	[illegible]
-19	2	17	4
0	3	46	54
1	3	469	462
-1	3	363	337
2	3	116	112
-2	3	153	150
3	3	289	287
-3	3	341	350
4	3	188	209
-4	3	135	161
5	3	177	139
-5	3	330	347
6	3	209	205
-6	3	216	233
7	3	191	222
-7	3	248	266
8	3	211	206
-8	3	216	221
9	3	212	197
-9	3	187	198
10	3	73	83
-10	3	76	86
11	3	82	57
-11	3	42	46
12	3	28	16
-12	3	76	87
13	3	76	63
-13	3	98	102
14	3	15	22
-14	3	84	60
15	3	40	40
-15	3	96	67
16	3	65	62
-16	3	57	41
17	3	80	65
-17	3	54	45
18	3	60	56
-18	3	36	34
0	4	317	292
1	4	199	216
-1	4	384	391
2	4	321	287
-2	4	128	111
3	4	128	126
-3	4	336	282
4	4	203	190
-4	4	244	238
5	4	167	157
-5	4	182	157
6	4	146	149
-6	4	182	168
7	4	175	197
-7	4	56	55
8	4	156	168
-8	4	94	85
9	4	113	105
-9	4	133	150
10	4	134	133
-10	4	87	88
11	4	105	98
-11	4	136	119
12	4	111	98
-12	4	60	65
13	4	103	91
-13	4	145	119
14	4	37	34
-14	4	140	104
15	4	57	50
-15	4	82	62
16	4	30	25
-16	4	35	33
17	4	26	22
-17	4	37	27
-18	4	15	19
0	5	182	177
1	5	151	145
-1	5	192	166
2	5	131	115
-2	5	192	178
3	5	167	165
-3	5	202	195
4	5	326	312
-4	5	120	104
5	5	226	200
-5	5	219	200
6	5	96	86
-6	5	104	103
7	5	153	143
-7	5	113	103
8	5	67	66
-8	5	178	183
9	5	23	23
-9	5	47	43
10	5	35	34
-10	5	172	164
11	5	31	31
-11	5	71	60
12	5	8*	6
-12	5	78	75
13	5	54	38
-13	5	44	30
14	5	7*	26
-14	5	8*	8
15	5	58	46
-15	5	38	35
-16	5	61	53
-17	5	47	60
0	6	100	108
1	6	225	187
-1	6	89	79
2	6	160	128
-2	6	123	117
3	6	43	54
-3	6	195	160
4	6	169	121
-4	6	94	74
5	6	37	34
-5	6	81	67
6	6	29	37
-6	6	86	72
7	6	82	66
-7	6	30	36
8	6	85	73
-8	6	145	122
9	6	99	67
-9	6	58	44
10	6	41	38
-10	6	107	77
11	6	109	78
-11	6	46	31
12	6	66	59
-12	6	100	89
13	6	86	64
-13	6	66	58
14	6	37	38
-14	6	69	49
-15	6	25	13
0	7	141	92
1	7	130	76
-1	7	44	44
2	7	137	90
-2	7	116	67
3	7	131	104
-3	7	201	123
4	7	145	99
-4	7	36	22
5	7	92	63
-5	7	209	119
6	7	74	61
-6	7	115	80
7	7	50	37
-7	7	92	60
8	7	72	61
-8	7	44	39
9	7	50	28
-9	7	55	50
10	7	13	13
-10	7	21	8
11	7	28	10
-11	7	19	13
12	7	36	28
-12	7	31	29
-13	7	33	31
0	8	73	53
1	8	117	70
-1	8	123	77
2	8	84	55
-2	8	50	30
3	8	49	27
-3	8	76	33
4	8	51	22
-4	8	83	69
5	8	44	25
-5	8	75	52
6	8	67	33
-6	8	44	28
7	8	58	51
-7	8	18	10
8	8	48	39
-8	8	70	52
9	8	45	33
-9	8	75	55
-10	8	22	15
-11	8	33	25
0	9	61	40
1	9	31	22
-1	9	50	30
2	9	41	14
-2	9	40	22
3	9	11	12
-3	9	32	16
4	9	73	53
-4	9	44	38
-5	9	60	46
-6	9	27	22
-7	9	32	39
K = 1			
0	0	283	372
1	0	286	194
-1	0	191	182
2	0	494	496
-2	0	613	517
3	0	658	652
-3	0	241	247
4	0	484	530
-4	0	66	60
5	0	363	368
-5	0	434	454
6	0	255	281
-6	0	532	475
7	0	111	107
-7	0	557	514
8	0	146	170
-8	0	133	131
9	0	152	162
-9	0	106	114
10	0	126	150
-10	0	220	229
11	0	56	67
-11	0	96	96
12	0	119	134
-12	0	181	157
13	0	37	41
-13	0	101	102
14	0	107	111
-14	0	58	43
15	0	67	60
-15	0	47	50
16	0	102	93
-16	0	120	86
17	0	66	59
-17	0	23	27
18	0	46	33
-18	0	71	57
19	0	18	24
-19	0	24	23
0	1	1064	1063
0	-1	257	318
1	1	227	208
-1	1	545	585
1	-1	205	232
-1	-1	546	601
2	1	294	358
-2	1	488	510
2	-1	417	407
-2	-1	216	207
3	1	406	346
-3	1	534	512
3	-1	157	172
-3	-1	472	588
4	1	460	452
-4	1	670	631
4	-1	239	241
-4	-1	320	332
5	1	151	151
-5	1	284	293
5	-1	227	217
-5	-1	375	357
6	1	290	299
-6	1	85	103
6	-1	455	468
-6	-1	219	207
7	1	130	155
-7	1	325	369
7	-1	320	354
-7	-1	167	146
8	1	258	285
-8	1	223	211
8	-1	120	127
-8	-1	116	115
9	1	218	254
-9	1	85	93
9	-1	250	289
-9	-1	41	55
10	1	139	151
-10	1	167	162
10	-1	116	107
-10	-1	85	85
11	1	146	154
-11	1	55	66
11	-1	186	228
-11	-1	123	116
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11	-1	118	94
-11	-1	23	26
12	1	24	19
-12	1	48	47
12	-1	87	52
-12	-1	97	101
13	1	10*	11
-13	1	155	128
13	-1	69	57
-13	-1	75	72
14	1	37	39
-14	1	62	53
14	-1	24	41
-14	-1	94	99
15	1	31	10
-15	1	71	60
15	-1	32	21
-15	-1	45	51
16	1	4	14
-16	1	67	69
16	-1	28	2
-16	-1	59	62
-17	1	58	56
-17	-1	33	36
-18	1	43	42
-18	-1	34	38
0	2	440	324
0	-2	253	197
1	2	374	285
-1	2	136	114
1	-2	210	150
-1	-2	190	131
2	2	41	51
-2	2	234	158
2	-2	623	417
-2	-2	246	206
3	2	284	193
-3	2	162	136
3	-2	113	96
-3	-2	246	159
4	2	118	97
-4	2	62	63
4	-2	615	355
-4	-2	80	66
5	2	69	52
-5	2	123	114
5	-2	233	197
-5	-2	35	26
6	2	135	117
-6	2	127	103
6	-2	317	232
-6	-2	206	164
7	2	158	128
-7	2	286	243
7	-2	234	182
-7	-2	231	251
8	2	86	71
-8	2	142	143
8	-2	112	100
-8	-2	112	128
9	2	151	107
-9	2	93	94
9	-2	111	110
-9	-2	117	116
10	2	30	45
-10	2	92	93
10	-2	109	91
-10	-2	203	195
11	2	84	61
-11	2	117	108
11	-2	58	62
-11	-2	60	56
12	2	49	26
-12	2	132	107
12	-2	89	66
-12	-2	120	126
13	2	75	58
-13	2	29	48
13	-2	47	48
-13	-2	12	9
14	2	97	73
-14	2	42	27
14	-2	116	78
-14	-2	25	21
15	2	31	32
-15	2	55	47
15	-2	54	43
-15	-2	47	39
-16	2	22	19
16	-2	33	45
-16	-2	19	16
-17	2	31	33
-17	-2	26	29
-18	2	11	13
-18	-2	4	19
0	3	93	81
0	-3	255	150
1	3	162	159
-1	3	97	91
1	-3	277	168
-1	-3	478	297
2	3	69	68
-2	3	240	208
2	-3	248	188
-2	-3	237	142
3	3	82	103
-3	3	275	224
3	-3	289	171
-3	-3	480	362
4	3	63	70
-4	3	98	61
4	-3	156	95
-4	-3	294	238
5	3	124	124
-5	3	128	100
5	-3	184	123
-5	-3	239	179
6	3	139	180
-6	3	142	134
6	-3	98	57
-6	-3	196	134
7	3	89	107
-7	3	82	85
7	-3	52	36
-7	-3	193	123
8	3	98	119
-8	3	115	99
8	-3	197	173
-8	-3	87	51
9	3	130	152
-9	3	56	48
9	-3	176	170
-9	-3	40	31
10	3	21	15
-10	3	83	86
10	-3	121	130
-10	-3	120	87
11	3	59	62
-11	3	151	136
11	-3	126	115
-11	-3	108	85
12	3	19*	15
-12	3	83	85
12	-3	42	33
-12	-3	110	92
13	3	38	23
-13	3	57	50
13	-3	58	49
-13	-3	78	66
14	3	28	24
-14	3	45	43
14	-3	29	21
-14	-3	60	51
-15	3	79	63
15	-3	30	30
-15	-3	92	77
-16	3	15	18
-16	-3	56	51
-17	3	27	14
-17	-3	19	20
0	4	36	45
0	-4	213	146
1	4	171	172
-1	4	94	75
1	-4	215	157
-1	-4	158	106
2	4	140	146
-2	4	63	63
2	-4	190	115
-2	-4	115	91
3	4	111	86
-3	4	114	125
3	-4	323	231
-3	-4	150	78
4	4	17*	38
-4	4	128	139
4	-4	300	197
-4	-4	101	65
5	4	138	134
-5	4	67	85
5	-4	233	160
-5	-4	225	162
6	4	90	66
-6	4	156	149
6	-4	301	227
-6	-4	125	115
7	4	36	9
-7	4	67	61
7	-4	83	62
-7	-4	180	168
8	4	58	27
-8	4	76	77
8	-4	44	11
-8	-4	171	171
9	4	38	40
-9	4	107	120
9	-4	94	77
-9	-4	73	86
10	4	40	45
-10	4	74	82
10	-4	19*	19
-10	-4	99	95
11	4	44	51
-11	4	35	41
11	-4	79	53
-11	-4	102	104
12	4	29	16
-12	4	74	87
12	-4	69	51

Table 3 (cont.)

H	L	$10F_o$	$10F_c$

The table consists of nine columns of structure-factor data, each headed by H, L, $10F_o$, $10F_c$. Section dividers appearing within the columns read: **K = 5**, **K = 6**, **K = 7**, **K = 8**, and **K = 9**.

Table 4. *Reflexions used to determine the absolute configuration*

	Calculated		Observed	
$h0l$	$F^2 (h0l)$	$F^2 (\bar{h}0\bar{l})$	$I(h0l)$	$I(\bar{h}0\bar{l})$
1001	82·76	117·84	<	
$\bar{1}\bar{2}01$	226·83	258·65	<	
$\bar{3}02$	314·71	332·05	<	
602	12·48	33·86	≪	
802	48·56	27·33	≫	
$\bar{8}02$	75·91	111·92	<	
203	158·45	104·08	>	
$\bar{2}03$	197·11	264·42	<	
$\bar{2}04$	141·80	107·67	≫	
305	303·99	248·16	>	
006	131·78	107·53	>	
$\bar{1}06$	75·38	53·62	>	

C(7) carbonyl band typical of cyclic amino-ketones which are capable of transannular interaction (Leonard, 1956), and by the X-ray structure analysis which shows C(7) and N to be bonded and C(7)–O(1) to correspond to an enolic rather than carbonyl grouping. The proton from this group and the two from the water molecule are used to form three hydrogen bonds: two between a water molecule and the sulphonate oxygen atoms of neighbouring anions and the third between O(1) and the water molecule for which the donor–acceptor scheme is most probably:

O(10)

H

O(12)········H—O(1)

H

O(9)
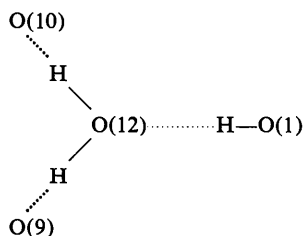
All other intermolecular contacts are of the van der Waals type, those that are shorter than 3·6 Å being listed in Table 7.

The intramolecular bonded distances for both cation and anion are listed in Table 5 and the bond angles in Table 6, the average standard deviations being about 0·02 Å and 1·3° in all cases. Only the C(7)–N bond (1·64 Å) shows a significant difference from the characteristic value of 1·52 Å suggested by Hamilton *et al.* (1962) for C_{te}–N. This lengthening by as much as 6σ is particularly interesting since this is the labile bond which is broken to form the partial bond CH_3–$N^{\delta+}$--- C=$O^{\delta-}$ (Leonard, 1956) when the free base, retusamine, is regenerated. We have not found it possible to rationalize this elongation in any quantitative way but consider that it must be the result of residual electronic factors associated with the *N*-methyl–carbonyl transannular interaction which occurs in the free base (Wunderlich, 1962).

Normal bond lengths have been found for the ring fusion C–N bond in both thelopogine methiodide (1·51 Å) (Fridrichsons & Mathieson, 1963) and jacobine bromohydrin (1·51 Å and 1·49 Å) (Fridrichsons, Ma-

thieson & Sutor, 1963) in which the central C–N bond of the retronecine nucleus is not susceptible to fission. The possibility that the effect is due to strain in the molecule is ruled out by the fact that the other bond distances and all angles in the two fused five-membered rings are quite normal.

Comparable elongations occur in the square coordinated platinum-olefin series (Basolo & Pearson, 1962). For example in Zeise's salt (Wunderlich & Mellor, 1954), $K[PtCl_3(CH_2=CH_2)] \cdot H_2O$, the distance between the Pt atom and the Cl atom opposite the

Table 5. *Interatomic distances*

C_{te}–C_{te}* (characteristic value $= 1·526 \pm 0·002$ Å)†		C_{te}–OH (characteristic value $= 1·43 \pm 0·01$ Å)	
C(4)—C(5)	1·50 Å	C(7)–O(1)	1·38 Å
C(5)—C(6)	1·50		
C(6)—C(7)	1·56	C_{tr}–O (ester)	
C(11)—C(12)	1·54	(characteristic value	
C(12)—C(13)	1·52	$= 1·34 \pm 0·01$ Å)	
C(11)—C(14)	1·53	C(10)–O(2)	1·32
C(14)—C(15)	1·55	C(18)–O(7)	1·31
C(14)—C(16)	1·53	C(19)–O(5)	1·32
C(16)—C(17)	1·55		
		C_{te}–O (ester)	
C(20)—C(21)	1·53	(characteristic value	
C(21)—C(26)	1·52	$= 1·43 \pm 0·01$ Å)	
C(21)—C(27)	1·59	C(6)–O(2)	1·44
C(23)—C(24)	1·52	C(8)–O(7)	1·44
C(24)—C(25)	1·58	C(16)–O(5)	1·46
C(24)—C(27)	1·56		
C(25)—C(26)	1·58	C_{te}–N^+	
C(27)—C(28)	1·54	(characteristic value	
C(27)—C(29)	1·49	$= 1·52 \pm 0·03$ Å)	
		C(3)–N	1·55
C_{te}–C_{tr}*		C(4)–N	1·52
(characteristic value		C(9)–N	1·49
$= 1·501 \pm 0·004$ Å)		C(7)–N	1·64
C(1)—C(7)	1·49		
C(1)—C(8)	1·47	C_{te}–S	
C(2)—C(3)	1·45	(characteristic value	
C(10)—C(11)	1·50	$= 1·80 \pm 0·01$ Å)	
C(11)—C(19)	1·57	C(29)–S	1·83
C(16)—C(18)	1·49		
		C_{te}–Br	
C(21)—C(22)	1·53	(characteristic value	
C(22)—C(23)	1·54	$= 1·937 \pm 0·003$ Å)	
		C(23)–Br	1·99
$C_{tr}=C_{tr}$			
(characteristic value		S_{te}–O	
$= 1·335 \pm 0·010$ Å)		(characteristic value	
C(1)–C(2)	1·33	$= 1·43 \pm 0·01$ Å)	
		S–O(9)	1·43
$C_{tr}=O$ (carboxyl)		S–O(10)	1·48
(characteristic value		S–O(11)	1·47
$= 1·233 \pm 0·005$ Å)			
C(10)–O(3)	1·24	O---HO	
C(18)–O(6)	1·25	(characteristic value	
C(19)–O(4)	1·22	$= 2·76$ Å in ice)	
C(22)–O(8)	1·20	O(1)—O(12)	2·63
		O(9)—O(12)	2·79
		O(10)–O(12)	2·83

* te = tetrahedral and tr = trigonal corresponding to sp^3 and sp^2 hybridization respectively.

† The characteristic values quoted are those given by Hamilton *et al.* (1962) for C_{te}–N^+, by Lide (1962) for C–C and C–O bonds and by Sutton (1958) for the other cases.

ethylene molecule is 0·10 Å longer than the two other Pt–Cl bond lengths. This is compatible with the known labile character of the 'trans' chlorine atom.

It is of interest to note that the conformation of the pyrrolizidine ring system in the retusamine cation is different from that found for jacobine and thelopogine. C(5) is cis to C(1)=C(2) in retusamine [endo-buckling of ring NC(7)C(6)C(5)C(4) with respect to ring NC(3)C(2)C(1)C(7)] while it lies in the trans position (exo-buckling) in both other compounds. It is possible

that this difference is simply due to steric effects arising from the bulky methyl group at the nitrogen atom and the hydroxyl group at C(7). Furthermore, in retronecine the nuclear magnetic resonance data are interpretable only on the basis of exo-buckling at C(5) (Culvenor, Heffernan & Woods, 1965).

The γ-lactone group is planar within the limits of error, conforming to the generalizations recently put forward (Mathieson & Taylor, 1961; Jeffrey & Kim, 1966) and the C–O bond α to the carbonyl group in

(a)

(b)
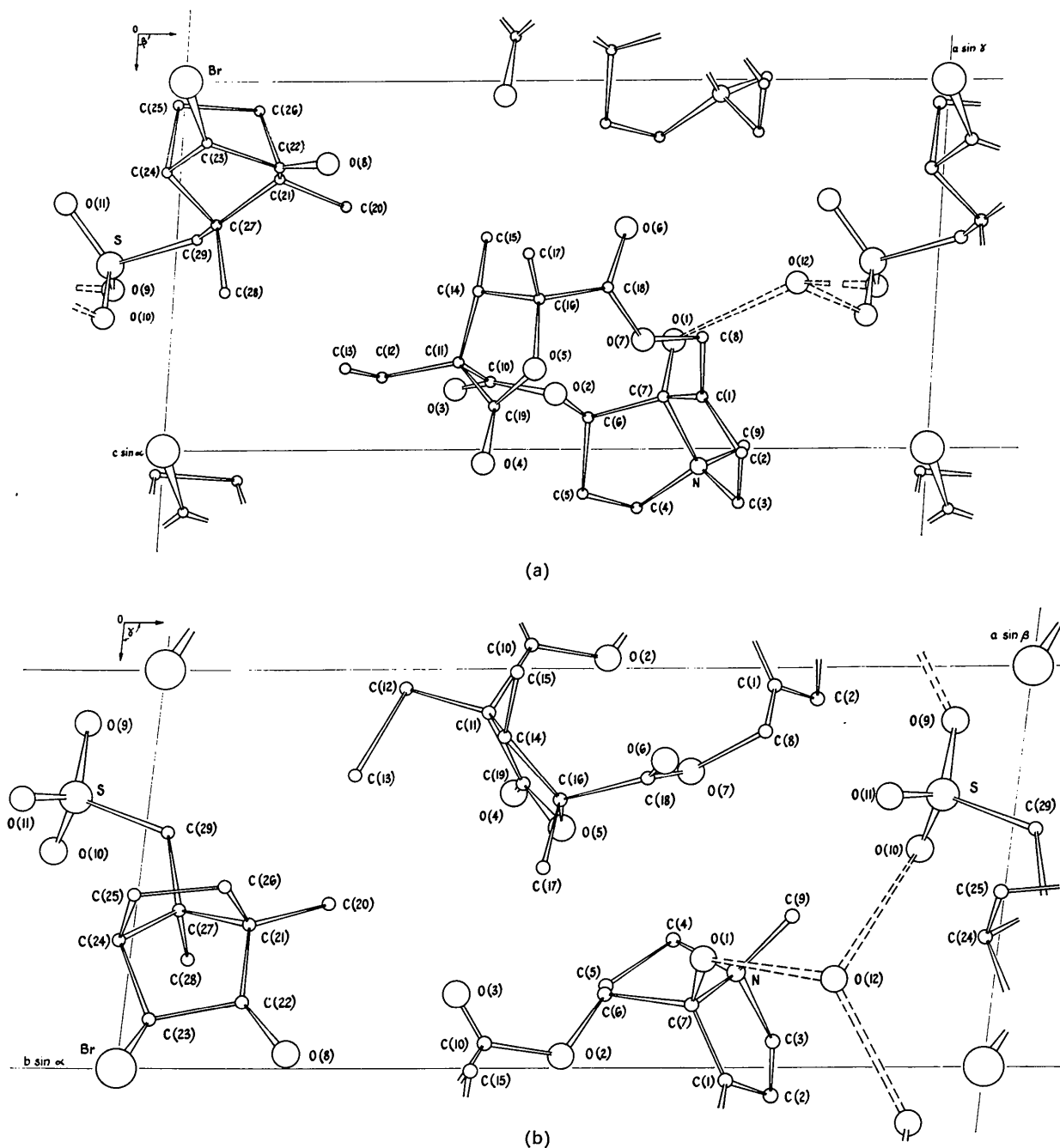
Fig. 1. Perspective drawing of the contents of the unit cell viewed (a) along the b axis and (b) along the c axis.

A C 23 – 12*

Table 6. *Bond angles*

Retusamine cation angles

C(2)—C(1)—C(7)	111·9°	C(11)-C(12)-C(13)	114·5°
C(2)—C(1)—C(8)	125·6	C(11)-C(14)-C(15)	114·6
C(7)—C(1)—C(8)	121·8	C(11)-C(14)-C(16)	106·4
C(1)—C(2)—C(3)	116·0	C(15)-C(14)-C(16)	116·3
C(2)—C(3)—N	102·5	C(14)-C(16)-C(17)	110·7
N——C(4)—C(5)	102·9	C(14)-C(16)-C(18)	118·9
C(4)—C(5)—C(6)	103·1	C(14)-C(16)-O(5)	104·0
C(5)—C(6)—C(7)	110·1	C(17)-C(16)-C(18)	108·4
C(5)—C(6)—O(2)	112·1	C(17)-C(16)-O(5)	105·6
C(7)—C(6)—O(2)	107·8	C(18)-C(16)-O(5)	108·4
C(1)—C(7)—C(6)	120·4	C(16)-C(18)-O(6)	119·3
C(1)—C(7)—N	101·2	C(16)-C(18)-O(7)	115·3
C(1)—C(7)—O(1)	116·0	O(6)-C(18)-O(7)	124·7
C(6)—C(7)—N	99·9	C(11)-C(19)-O(4)	126·1
C(6)—C(7)—O(1)	106·6	C(11)-C(19)-O(5)	110·6
N——C(7)—O(1)	111·2	O(4)—C(19)-O(5)	123·3
C(1)—C(8)—O(7)	108·0	C(6)—O(2)—C(10)	116·1
C(11)-C(10)-O(2)	112·9	C(16)-O(5)—C(19)	113·2
C(11)-C(10)-O(3)	123·2	C(8)—O(7)—C(18)	120·0
O(2)—C(10)-O(3)	123·8	C(3)—N——C(4)	110·5
C(10)-C(11)-C(12)	110·1	C(3)—N——C(7)	105·0
C(10)-C(11)-C(14)	113·1	C(3)—N——C(9)	111·5
C(10)-C(11)-C(19)	107·7	C(4)—N——C(7)	106·5
C(12)-C(11)-C(14)	114·8	C(4)—N——C(9)	111·6
C(12)-C(11)-C(19)	109·4	C(7)—N——C(9)	111·3
C(14)-C(11)-C(19)	101·1		

Bromocamphorsulphonate angles

C(20)-C(21)-C(22)	113·4°	C(24)-C(25)-C(16)	100·1°
C(20)-C(21)-C(26)	114·1	C(21)-C(26)-C(25)	106·2
C(20)-C(21)-C(27)	119·4	C(21)-C(27)-C(24)	93·1
C(22)-C(21)-C(16)	104·0	C(21)-C(27)-C(28)	110·6
C(22)-C(21)-C(27)	98·8	C(21)-C(27)-C(29)	109·4
C(26)-C(21)-C(27)	105·0	C(24)-C(27)-C(28)	116·9
C(21)-C(22)-C(23)	104·3	C(24)-C(27)-C(29)	114·2
C(21)-C(22)-O(8)	129·4	C(28)-C(27)-C(29)	111·0
C(23)-C(22)-O(8)	126·2	C(27)-C(29)-S	116·2
C(22)-C(23)-C(24)	103·7	C(29)-S——O(9)	104·3
C(22)-C(23)-Br	110·0	C(29)-S——O(10)	107·0
C(24)-C(23)-Br	114·1	C(29)-S——O(11)	107·9
C(23)-C(24)-C(25)	108·4	O(9)—S——O(10)	112·3
C(23)-C(24)-C(27)	98·5	O(9)—S——O(11)	113·1
C(25)-C(24)-C(27)	105·4	O(10)-S——O(11)	111·2

Hydrogen bond angles

C(7)—O(1)—O(12)	114·9°	O(1)—O(12)-O(9)	123·3°
S——O(9)—O(12)	138·6	O(1)—O(12)-O(10)	103·6
S——O(10)-O(12)	122·4	O(9)—O(12)-O(10)	119·8

Table 7. *Intermolecular distances
equal to or less than 3·60 Å*

Primed and doubly primed atoms belong to molecules related by $-b$ and $+c$ respectively to that containing the unprimed atoms.

O(1)—O(7′)	3·36	O(9)—C(8)	3·58
O(1)—O(5′)	3·47	O(10)-C(8)	3·46
O(1)—C(18′)	3·49	O(11)-C(2)	3·10
O(1)—C(17′)	3·58	O(11)-C(3)	3·20
C(6)—O(5′)	3·18	C(9)—C(25)	3·60
O(4)—C(15″)	3·58	C(15)-O(8)	3·46
O(10)-C(25″)	3·43	O(12)-C(9)	3·55
O(9)—Br″	3·56	O(12)-C(7)	3·45
O(4)—C(17″)	3·37	O(12)-C(3)	3·33
O(3)—O(5′)	3·29	O(12)-C(1)	3·47
C(4)—C(17″)	3·58	O(12)-C(8)	3·53

both the lactone and ester groups is about 0·1 Å shorter than the β C–O bond length, a difference to be expected from the possible resonance forms in esters.

As with other esters of secondary alcohols (Mathieson, 1965; Culvenor, 1966), the planar ester group C(11)–C(10)–O(2)–C(6) and the hydrogen atom on C(6)

O(3)

are in the eclipsed conformation with O(3) *cis* to the hydrogen atom. This restriction, and those imposed by the γ-lactone ring, the planarity of the primary ester group and the conformation of the pyrrolizidine nucleus itself, are sufficient to determine the shape of the molecule. There result two very short intramolecular

contacts involving the ether oxygen atoms, namely between O(2) and O(7) (2·71 Å) and between O(5) and O(7) (2·54 Å). The shape of the jacobine molecule (Fridrichsons, Mathieson & Sutor, 1963) is apparently also governed by the ester group conformations. In an alkaloid derived from *Senecio kirkii* (Dodson & Hall, 1966), the corresponding secondary ester group conformation is staggered and the ether oxygen atom separation is about 3·1 Å.

The chemical and structural relationships between the retusamine cation and those of the free base have already been discussed (Wunderlich, 1962).

Turning now to the anion molecule, we find that as in 3-bromo-, 3-chloro- and 3-cyano-camphor, the bromine atom in the bromocamphorsulphonate anion is in the *endo* (α' or *trans*) direction. This is in contrast to the structure of 10-bromo-2-chloro-2-nitrosocamphane (Ferguson, Fritchie, Robertson & Sim, 1961) and 2-bromo-2-nitrocamphane (Brueckner, Hamor, Robertson & Sim, 1962) where the Cl and Br atoms are in the *exo* (α or *cis*) positions.

The bond lengths appear normal though the C–Br distance of $1·99 \pm 0·02$ Å is somewhat longer than the average value of 1·94 Å quoted for alkyl bromides (Sutton, 1958). Comparably long distances have been found in 5′-bromo-5′-deoxythymidine (Huber, 1957) and in dibromomenthone (Wunderlich & Lipscomb, 1960).

Of the bond angles, mention should be made of the bridgehead C(21),C(27),C(24) angle of 93° which is in good agreement with the values of 95 and 91 and 93° found in the two camphane derivatives referred to above. Furthermore all ring valence angles are less than the tetrahedral angle of 109°28′ while all *exo*-cyclic angles are greater, a feature also noted by Brueckner *et al.* (1962) and discussed in detail by Sim (1965).

The structures of the three α'-substituted camphors (Wiebenga & Krom, 1946) are not sufficiently accurate for meaningful comparisons of bond lengths and angles to be made.

The other feature of stereochemical interest is that the sulphonate group is in the *trans-π* (9) position and not in the *cis-π* (8) position as proposed originally by Kipping & Pope (1893) and tacitly accepted by many investigators since then. It follows then that compounds which can be derived from or converted into bromocamphorsulphonic acid such as camphor-π-sulphonic acid and its derivatives and also the π-halo-camphors must have the same *trans-π* configuration.

References

BASOLO, F. & PEARSON, R. G. (1962). *Progr. Inorg. Chem.* **4**, 381.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271.

BRUECKNER, D. A., HAMOR, T. A., ROBERTSON, J. M. & SIM, G. A. (1962). *J. Chem. Soc.* p. 799.

BUSING, W. R. & LEVY, H. A. (1959). Report 59-4-37, Oak Ridge National Laboratory, Tennessee.

CULVENOR, C. C. J. (1966). *Tetrahedron Letters*, **10**, 1091.

CULVENOR, C. C. J., HEFFERNAN, M. L. & WOODS, W. G. (1965). *Aust. J. Chem.* **18**, 1605.

CULVENOR, C. C. J. & SMITH, L. W. (1957). *Aust. J. Chem.* **10**, 464.

DAUBEN, C. H. & TEMPLETON, C. D. (1955). *Acta Cryst.* **8**, 841.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

DODSON, G. G. & HALL, D. (1966). *Acta Cryst.* **20**, 42.

FERGUSON, G., FRITCHIE, C. J., ROBERTSON, J. M. & SIM, G. A. (1961). *J. Chem. Soc.* p.1976.

FREDGA, A. & MIETTINEN, J. K. (1947). *Acta Chem. Scand.* **1**, 371.

FRIDRICHSONS, J. & MATHIESON, A. McL. (1963). *Acta Cryst.* **16**, 206.

FRIDRICHSONS, J., MATHIESON, A. McL. & SUTOR, D. J. (1963). *Acta Cryst.* **16**, 1075.

HAMILTON, J. A., HAMOR, T. A., ROBERTSON, J. M. & SIM, G. A. (1962). *J. Chem. Soc.* p. 5061.

HUBER, M. (1957). *Acta Cryst.* **10**, 129.

JEFFREY, G. A. & KIM, S. H. (1966). *Chem. Comm.* p. 211.

KIPPING, F. S. & POPE, W. J. (1893). *J. Chem. Soc.* **63**, 577.

LEONARD, N. J. (1956). *Rec. Chem. Progr.* **17**, 243.

LIDE, D. R. (1962). *Tetrahedron*, **17**, 125.

MATHIESON, A. McL. (1951). *J. Sci. Instrum.* **28**, 112.

MATHIESON, A. McL. (1965). *Tetrahedron Letters*, **46**, 4137.

MATHIESON, A. McL. & TAYLOR, J. C. (1961). *Tetrahedron Letters*, **17**, 590.

PEERDEMAN, A. F. (1956). *Acta Cryst.* **9**, 824.

PETERSON, S. W. (1955). *Nature, Lond.* **176**, 395.

SIM, G. A. (1965). *J. Chem. Soc.* p. 5974.

SIMONSEN, J. L. (1949). *The Terpenes*. Vol. II. Cambridge Univ. Press.

SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configurations in Molecules and Ions*. London: The Chemical Society.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

WIEBENGA, E. H. & KROM, C. J. (1946). *Rev. trav. chim. Pays-Bas*, **65**, 663.

WUNDERLICH, J. A. (1962). *Chem. and Ind.* p. 2089.

WUNDERLICH, J. A. (1967). *Acta Cryst.* **23**, 181.

WUNDERLICH, J. A. & LIPSCOMB, W. N. (1960). *Tetrahedron*, **11**, 219.

WUNDERLICH, J. A. & MELLOR, D. P. (1954). *Acta Cryst.* **7**, 130.

ZHDANOVICH, E. S. & MEN'SHIKOV, G. P. (1941). *J. Gen. Chem. Moscow*, **11**, 835.