X-Ray Study of the Molecular Structure of 4-Demethylhasubanonine *p*-Bromobenzenesulphonate

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Elucidation of the crystal structure of the title ester has established the parent alkaloid to be 4-demethylhasubanonine. In the alkaloid molecule, the five-membered ring containing the nitrogen atom has an envelope conformation with C(14) out-of-plane. The S–OC bond of the *p*-bromobenzenesulphonyl group is steeply inclined to the bromobenzene plane, and the conformation about the S–OC bond is gauche. The crystals are orthorhombic, space group $P2_12_12_1$, $Z = 4$ in a cell of dimensions $a = 8{\cdot}52$, $b = 24{\cdot}23$, $c = 12{\cdot}60$ Å. The structure was solved by Patterson and Fourier methods from photographic data and refined by least-squares techniques to R 11·3% for 1783 independent reflections.

SEVERAL alkaloids with anti-tumour activity have been obtained from the Indian shrub *Stephania hernandifolia*.[1] Recently Kupchan *et al.* isolated a new phenolic alkaloid from this source,[2] and we undertook an *X*-ray crystal structure analysis of the *p*-bromobenzenesulphonyl ester. The alkaloid proved to be 4-demethylhasubanonine, with constitution and stereochemistry shown in (1; R = H). The absolute configuration agrees with that assigned to hasubanonine (1; R = Me) on the basis of o.r.d. measurements,[3] and is the opposite of that encountered in the morphine series of alkaloids.[4] *X*-Ray determin-

TABLE 1

Atomic co-ordinates (as fractions of the cell edges), positional standard deviations (Å), and temperature factors (Å²)

	x	*y*	*z*	σ(*X*)	σ(*Y*)	σ(*Z*)	*B*
C(1)	0·9681	−0·6992	0·1749	0·017	0·016	0·017	4·1
C(2)	0·9624	−0·7388	0·2595	0·017	0·014	0·015	3·8
C(3)	1·1064	−0·7574	0·3037	0·015	0·013	0·014	3·2
C(4)	1·2482	−0·7355	0·2608	0·014	0·013	0·014	2·9
C(5)	1·5168	−0·6520	0·2360	0·013	0·012	0·013	2·7
C(6)	1·4430	−0·6016	0·2879	0·012	0·011	0·013	2·6
C(7)	1·3749	−0·5605	0·2211	0·013	0·012	0·014	3·0
C(8)	1·3550	−0·5691	0·1161	0·015	0·014	0·014	3·5
C(9)	1·2604	−0·6383	−0·0161	0·015	0·014	0·015	3·6
C(10)	1·1012	−0·6392	0·0399	0·016	0·014	0·015	3·8
C(11)	1·1110	−0·6801	0·1341	0·014	0·012	0·013	2·7
C(12)	1·2551	−0·6970	0·1800	0·013	0·012	0·013	2·6
C(13)	1·4151	−0·6733	0·1419	0·012	0·011	0·013	2·5
C(14)	1·3947	−0·6248	0·0616	0·015	0·012	0·013	3·1
C(15)	1·5140	−0·7142	0·0752	0·015	0·014	0·015	3·4
C(16)	1·5946	−0·6815	−0·0099	0·015	0·013	0·014	3·4
C(17)	1·5815	−0·5857	−0·0752	0·019	0·019	0·019	5·4
C(18)	1·2572	−0·4756	0·0683	0·020	0·018	0·020	5·3
C(19)	1·4502	−0·4766	0·3090	0·021	0·020	0·021	5·7
C(20)	0·9718	−0·8129	0·4331	0·019	0·018	0·018	5·0
C(21)	1·2991	−0·9209	0·5061	0·019	0·016	0·017	4·3
C(22)	1·4042	−0·9105	0·5947	0·015	0·014	0·014	3·5
C(23)	1·5218	−0·8707	0·5839	0·019	0·017	0·018	4·6
C(24)	1·5396	−0·8425	0·4889	0·015	0·014	0·014	3·2
C(25)	1·4335	−0·8522	0·4050	0·014	0·013	0·015	3·1
C(26)	1·3135	−0·8920	0·4139	0·017	0·014	0·016	4·0
O(1)	1·3628	−0·8411	0·2042	0·011	0·010	0·011	4·2
O(2)	1·6211	−0·8083	0·2730	0·012	0·011	0·011	4·5
O(3)	1·3866	−0·7555	0·3105	0·010	0·008	0·009	2·9
O(4)	1·1189	−0·7913	0·3859	0·012	0·011	0·010	4·2
O(5)	1·4526	−0·5947	0·3827	0·012	0·011	0·011	4·2
O(6)	1·3268	−0·5130	0·2678	0·011	0·010	0·011	4·0
O(7)	1·2983	−0·5335	0·0413	0·012	0·010	0·011	3·9
N	1·5551	−0·6237	0·0142	0·013	0·012	0·012	3·6
S	1·4560	−0·8165	0·2864	0·004	0·003	0·004	†
Br	1·3840	−0·9495	0·7217	0·002	0·002	0·002	†

† The bromine and sulphur atoms were assigned anisotropic temperature factors of the form: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. The final values of the b_{ij} are:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br	0·0272	0·0016	0·0073	0·0011	0·0020	0·0019
S	0·0180	0·0011	0·0059	0·0004	−0·0009	0·0004

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[2] S. M. Kupchan, M. I. Suffness, D. N. J. White, A. T. McPhail, and G. A. Sim, *J. Org. Chem.*, 1968, **33**, 4529.

[3] M. Tomita, T. Ibuka, Y. Inubushi, Y. Watanabe, and M. Matsui, *Tetrahedron Letters*, 1964, 2937.

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ations of the absolute stereochemistries of acutumine[5] and kreysiginine[6] have shown that in these alkaloids also the heterocyclic ring containing the nitrogen atom is on the α-face of the molecule.

The atomic co-ordinates obtained from the *X*-ray analysis of 4-demethylhasubanonine *p*-bromobenzenesulphonate are listed in Table 1. The molecular dimensions are tabulated in Table 2 and the intermolecular contacts in Table 3. Figure 1 provides a view of the molecular structure and Figure 2 a view of the arrangement of molecules in the crystal.

Ring B adopts a distorted half-chair conformation in which C(9) and C(14) are displaced by 0·54 and −0·30 Å from the mean plane through C(10), C(13), and the carbon atoms of ring A. These displacements may be

TABLE 2

Molecular dimensions

(*a*) Bond lengths (Å)

Br–C(22)	1·87(0·014)	C(4)–C(12)	1·38(0·018)
S–O(1)	1·43(0·011)	C(5)–C(6)	1·52(0·017)
S–O(2)	1·43(0·012)	C(6)–C(7)	1·43(0·017)
S–O(3)	1·62(0·010)	C(7)–C(8)	1·35(0·020)
S–C(25)	1·74(0·015)	C(9)–C(14)	1·54(0·021)
O(3)–C(4)	1·42(0·016)	C(10)–C(9)	1·53(0·022)
O(4)–C(3)	1·33(0·017)	C(11)–C(10)	1·55(0·020)
O(4)–C(20)	1·48(0·022)	C(11)–C(12)	1·42(0·018)
O(5)–C(6)	1·21(0·017)	C(12)–C(13)	1·56(0·018)
O(6)–C(7)	1·36(0·016)	C(13)–C(5)	1·56(0·018)
O(6)–C(19)	1·47(0·023)	C(13)–C(15)	1·55(0·019)
O(7)–C(8)	1·37(0·018)	C(14)–C(8)	1·55(0·019)
O(7)–C(18)	1·49(0·021)	C(14)–C(13)	1·56(0·017)
N–C(14)	1·49(0·020)	C(15)–C(16)	1·50(0·020)
N–C(16)	1·47(0·018)	C(22)–C(21)	1·45(0·023)
N–C(17)	1·47(0·022)	C(22)–C(23)	1·40(0·023)
C(1)–C(11)	1·40(0·022)	C(23)–C(24)	1·39(0·023)
C(2)–C(1)	1·43(0·022)	C(24)–C(25)	1·41(0·021)
C(2)–C(3)	1·42(0·022)	C(25)–C(26)	1·41(0·021)
C(3)–C(4)	1·43(0·020)	C(26)–C(21)	1·36(0·023)

(*b*) Valency angles (deg.)

O(2)–S–O(1)	121·1(0·6)	C(9)–C(10)–C(11)	108·3(1·1)
O(3)–S–O(1)	108·1(0·6)	C(10)–C(11)–C(1)	116·5(1·0)
O(3)–S–O(2)	104·7(0·6)	C(10)–C(11)–C(12)	123·0(0·9)
C(25)–S–O(1)	110·7(0·7)	C(12)–C(11)–C(1)	120·4(0·9)
C(25)–S–O(2)	106·2(0·8)	C(11)–C(12)–C(4)	117·3(1·0)
C(25)–S–O(3)	104·6(0·6)	C(13)–C(12)–C(4)	121·0(1·0)
C(4)–O(3)–S	122·2(0·6)	C(13)–C(12)–C(11)	121·7(0·8)
C(20)–O(4)–C(3)	117·7(1·2)	C(5)–C(13)–C(12)	112·0(0·9)
C(7)–O(6)–C(19)	116·6(1·0)	C(5)–C(13)–C(14)	107·9(0·8)
C(8)–O(7)–C(18)	121·4(1·1)	C(14)–C(13)–C(12)	112·4(0·8)
C(16)–N–C(14)	106·0(0·9)	C(15)–C(13)–C(5)	108·8(0·8)
C(17)–N–C(14)	117·2(1·0)	C(15)–C(13)–C(12)	114·0(0·8)
C(17)–N–C(16)	113·7(1·1)	C(15)–C(13)–C(14)	101·0(0·8)
C(11)–C(1)–C(2)	121·6(1·2)	C(8)–C(14)–N	111·2(0·9)
C(1)–C(2)–C(3)	118·3(1·0)	C(9)–C(14)–N	115·5(0·9)
C(4)–C(3)–O(4)	117·3(1·1)	C(13)–C(14)–N	99·9(0·8)
C(2)–C(3)–O(4)	124·9(1·2)	C(8)–C(14)–C(9)	107·7(0·9)
C(2)–C(3)–C(4)	117·7(0·9)	C(8)–C(14)–C(13)	113·1(0·8)
C(3)–C(4)–O(3)	114·1(0·8)	C(13)–C(14)–C(9)	109·5(0·9)
C(12)–C(4)–O(3)	121·4(0·7)	C(16)–C(15)–C(13)	107·3(0·8)
C(12)–C(4)–C(3)	124·5(0·8)	C(15)–C(16)–N	104·5(0·9)
C(6)–C(5)–C(13)	111·2(0·8)	C(26)–C(21)–C(22)	120·6(1·0)
C(5)–C(6)–O(5)	120·5(1·0)	C(21)–C(22)–Br	120·9(0·7)
C(7)–C(6)–O(5)	120·9(0·9)	C(23)–C(22)–Br	119·9(0·7)
C(7)–C(6)–C(5)	118·4(0·9)	C(21)–C(22)–C(23)	119·2(1·2)
C(6)–C(7)–O(6)	117·4(0·9)	C(24)–C(23)–C(22)	120·2(1·2)
C(8)–C(7)–O(6)	121·2(0·9)	C(25)–C(24)–C(23)	119·7(1·1)
C(8)–C(7)–C(6)	121·4(0·9)	C(26)–C(25)–S	119·2(0·7)
C(7)–C(8)–O(7)	128·6(0·8)	C(24)–C(25)–S	119·5(0·7)
C(14)–C(8)–O(7)	108·6(0·9)	C(26)–C(25)–C(24)	121·2(1·0)
C(7)–C(8)–C(14)	122·8(0·8)	C(21)–C(26)–C(25)	119·1(1·1)
C(14)–C(9)–C(10)	111·7(1·0)		

TABLE 2 (*Continued*)

(*c*) Torsion angles (deg) *

O(1)–S–O(3)–C(4)	5	O(5)–C(6)–C(7)–O(6)	2
O(2)–S–O(3)–C(4)	135	O(5)–C(6)–C(7)–C(8)	−176
C(25)–S–O(3)–C(4)	−113	C(5)–C(6)–C(7)–O(6)	−172
O(1)–S–C(25)–C(24)	166	C(5)–C(6)–C(7)–C(8)	9
O(1)–S–C(25)–C(26)	−11	O(6)–C(7)–C(8)–O(7)	5
O(2)–S–C(25)–C(24)	33	O(6)–C(7)–C(8)–C(14)	−174
O(2)–S–C(25)–C(26)	−144	C(6)–C(7)–C(8)–O(7)	−177
O(3)–S–C(25)–C(24)	−77	C(6)–C(7)–C(8)–C(14)	4
O(3)–S–C(25)–C(26)	105	C(10)–C(9)–C(14)–N	179
S–O(3)–C(4)–C(3)	77	C(10)–C(9)–C(14)–C(8)	−56
S–O(3)–C(4)–C(12)	−105	C(10)–C(9)–C(14)–C(13)	68
C(20)–O(4)–C(3)–C(2)	2	C(11)–C(10)–C(9)–C(14)	−55
C(20)–O(4)–C(3)–C(4)	178	C(10)–C(11)–C(1)–C(2)	178
C(19)–O(6)–C(7)–C(6)	69	C(12)–C(11)–C(1)–C(2)	−4
C(19)–O(6)–C(7)–C(8)	−113	C(1)–C(11)–C(10)–C(9)	−161
C(18)–O(7)–C(8)–C(7)	4	C(12)–C(11)–C(10)–C(9)	20
C(18)–O(7)–C(8)–C(14)	−177	C(10)–C(11)–C(12)–C(13)	3
C(16)–N–C(14)–C(8)	166	C(10)–C(11)–C(12)–C(4)	−177
C(16)–N–C(14)–C(9)	−71	C(1)–C(11)–C(12)–C(13)	−176
C(16)–N–C(14)–C(13)	46	C(1)–C(11)–C(12)–C(4)	4
C(17)–N–C(14)–C(8)	−66	C(4)–C(12)–C(13)–C(5)	−50
C(17)–N–C(14)–C(9)	57	C(4)–C(12)–C(13)–C(14)	−172
C(17)–N–C(14)–C(13)	174	C(4)–C(12)–C(13)–C(15)	74
C(14)–N–C(16)–C(15)	−33	C(11)–C(12)–C(13)–C(5)	129
C(17)–N–C(16)–C(15)	−163	C(11)–C(12)–C(13)–C(14)	8
C(3)–C(2)–C(1)–C(11)	2	C(11)–C(12)–C(13)–C(15)	−107
O(4)–C(3)–C(2)–C(1)	176	C(14)–C(13)–C(5)–C(6)	−67
C(4)–C(3)–C(2)–C(1)	0	C(14)–C(13)–C(5)–C(6)	57
O(3)–C(4)–C(3)–O(4)	3	C(15)–C(13)–C(5)–C(6)	166
O(3)–C(4)–C(3)–C(2)	179	C(5)–C(13)–C(15)–C(16)	−91
C(12)–C(4)–C(3)–O(4)	−176	C(12)–C(13)–C(15)–C(16)	143
C(12)–C(4)–C(3)–C(2)	1	C(14)–C(13)–C(15)–C(16)	22
O(3)–C(4)–C(12)–C(11)	179	N–C(14)–C(8)–O(7)	85
O(3)–C(4)–C(12)–C(13)	−1	N–C(14)–C(8)–C(7)	−96
C(3)–C(4)–C(12)–C(11)	−3	C(9)–C(14)–C(8)–O(7)	−43
C(3)–C(4)–C(12)–C(13)	177	C(9)–C(14)–C(8)–C(7)	137
C(13)–C(5)–C(6)–O(5)	144	C(13)–C(14)–C(8)–O(7)	−164
C(13)–C(5)–C(6)–C(7)	−41	C(13)–C(14)–C(8)–C(7)	16
N–C(14)–C(13)–C(5)	74	Br–C(22)–C(21)–C(26)	179
N–C(14)–C(13)–C(12)	−162	C(23)–C(22)–C(21)–C(26)	−1
N–C(14)–C(13)–C(15)	−40	Br–C(22)–C(23)–C(24)	178
C(8)–C(14)–C(13)–C(5)	−45	C(21)–C(22)–C(23)–C(24)	−1
C(8)–C(14)–C(13)–C(12)	79	C(22)–C(23)–C(24)–C(25)	3
C(8)–C(14)–C(13)–C(15)	−159	C(23)–C(24)–C(25)–S	179
C(9)–C(14)–C(13)–C(5)	−165	C(23)–C(24)–C(25)–C(26)	−3
C(9)–C(14)–C(13)–C(12)	−41	S–C(25)–C(26)–C(21)	178
C(9)–C(14)–C(13)–C(15)	81	C(24)–C(25)–C(26)–C(21)	1
C(13)–C(15)–C(16)–N	5	C(25)–C(26)–C(21)–C(22)	3

* The angle A–B–C–D is positive if, when viewed along the B–C bond, atom A has to be rotated in a clockwise direction to eclipse atom D. The standard deviation of a torsion angle is *ca.* 1·5°.

(*d*) Equations * of mean planes through various sets of atoms and deviations (Å) of atoms from the planes. Atoms not included in the derivation of a plane are italicized

Plane (i): $0{\cdot}0439X - 0{\cdot}7545Y - 0{\cdot}6548Z = 11{\cdot}7338$

O(3) 0·04, O(4) −0·03, C(1) −0·03, C(2) 0·00, C(3) 0·02, C(4) 0·03, C(10) 0·04, C(11) 0·01, C(12) 0·01, C(13) −0·07, *C(9) 0·54*, *C(14) −0·30*

Plane (ii): $0{\cdot}9167X + 0{\cdot}3604Y - 0{\cdot}1726Z = 5{\cdot}3514$

O(6) −0·05, O(7) 0·04, C(6) 0·04, C(7) 0·01, C(8) 0·01, C(14) −0·05, *C(5) 0·29*, *C(13) −0·49*, *O(5) −0·03*

Plane (iii): $-0{\cdot}7796X - 0{\cdot}0882Y - 0{\cdot}6201Z = -9{\cdot}0876$

N −0·02, C(13) 0·02, C(15) −0·03, C(16) 0·03, *C(14) 0·68*

Plane (iv): $0{\cdot}6191X - 0{\cdot}7050Y - 0{\cdot}3450Z = 20{\cdot}3669$

Br 0·01, C(21) 0·00, C(22) 0·00, C(23) −0·01, C(24) 0·01, C(25) −0·02, C(26) 0·00, S 0·01, *O(1) 0·30*, *O(2) 0·80*, *O(3) −1·50*

* *X*, *Y*, and *Z* are orthogonal co-ordinates (Å)

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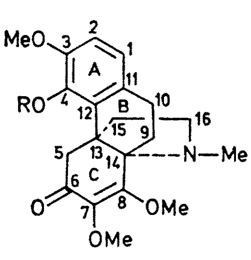
[5] M. Nishikawa, K. Kamiya, M. Tomita, Y. Okamato, T. Kikuchi, K. Osaki, Y. Tomiie, I. Nitta, and K. Goto, *J. Chem. Soc.* (*B*), 1968, 652.

[6] J. Fridrichsons, M. F. Mackay, and A. McL. Mathieson, *Tetrahedron Letters*, 1968, 2887.

compared with the values of ±0·43 Å deduced for ideal cyclohexene geometry.[7] Ring C also has a distorted half-chair conformation in which C(5) and C(13) are displaced by 0·29 and −0·49 Å from the plane through C(6), C(7), C(8), and C(14). The conjugated ethylenic and carbonyl functions deviate slightly from coplanarity, the C(5)–C(6)–C(7)–C(8) torsion angle being 9°. The conformation of the five-membered heterocyclic ring approximates closely to the envelope type with C(13), C(15), C(16), and N closely coplanar [the C(13)–C(15)–C(16)–N torsion angle is 5°] and C(14) displaced from the plane by 0·68 Å.



(1)

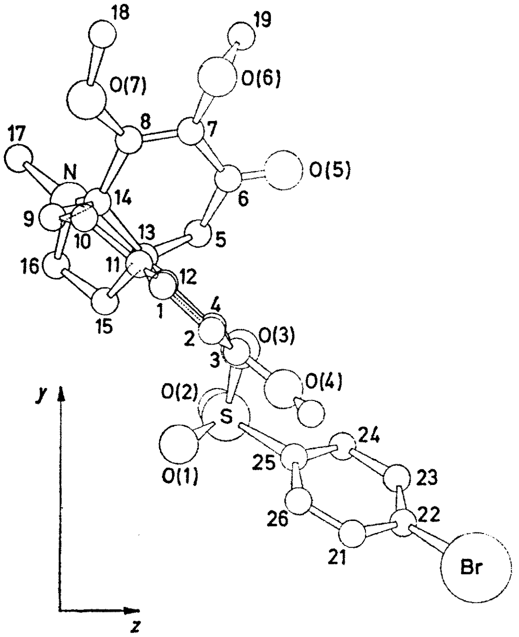


FIGURE 1 The molecular structure of 4-demethylhasubanonine *p*-bromobenzenesulphonate

TABLE 3

Intermolecular contacts ⩽3·80 Å

O(5) ··· C(20^{V})	3·23	O(2) ··· C(9^{IV})	3·68
O(5) ··· C(21^{V})	3·29	C(16) ··· C(11^{IV})	3·70
C(23) ··· C(2^{V})	3·35	O(3) ··· C(20^{V})	3·70
O(2) ··· C(2^{I})	3·36	C(18) ··· C(23^{III})	3·70
C(16) ··· O(1^{IV})	3·39	C(16) ··· C(1^{IV})	3·72
C(17) ··· O(^{1IV})	3·40	O(1) ··· C(10^{IV})	3·72
O(5) ··· C(18^{II})	3·40	C(18) ··· C(24^{III})	3·73
C(23) ··· C(3^{V})	3·49	C(23) ··· C(4^{V})	3·76
C(23) ··· C(1^{V})	3·51	C(15) ··· C(11^{IV})	3·77
O(2) ··· C(20^{I})	3·61	O(6) ··· O(7^{II})	3·78
C(24) ··· C(3^{V})	3·61	C(17) ··· Br^{III}	3·79
C(19) ··· O(7^{II})	3·62	C(23) ··· O(5^{V})	3·79
C(19) ··· O(1^{III})	3·65	C(24) ··· C(2^{V})	3·79
C(24) ··· O(4^{V})	3·67	C(15) ··· C(1^{IV})	3·80

The superscripts refer to the following transformations of the atomic co-ordinates:

I $1 + x, y, z$
II $\frac{5}{2} - x, -1 - y, \frac{1}{2} + z$
III $3 - x, \frac{1}{2} + y, \frac{1}{2} - z$
IV $\frac{1}{2} + x, -\frac{3}{2} - y, -z$
V $\frac{1}{2} + x, -\frac{3}{2} - y, 1 - z$

The *p*-bromobenzenesulphonate moiety adopts a conformation in which the S–OR bond is steeply inclined to the bromobenzene plane. This feature has general conformational significance, for in a number of *p*-bromobenzenesulphonates (2) the O(*b*)–S–C(*e*)–C(*f*) torsion angle lies in the range 62—91° (see Table 4). The C–S–O–C torsion angle in (1) is −113°, and in other derivatives values as diverse as 52—176° are found, most of the angles being representative of a gauche conformation about the S–OC bond. This is in marked contrast to carboxylate esters which invariably adopt a *trans*-conformation about the C–OC bond. The wide spread of

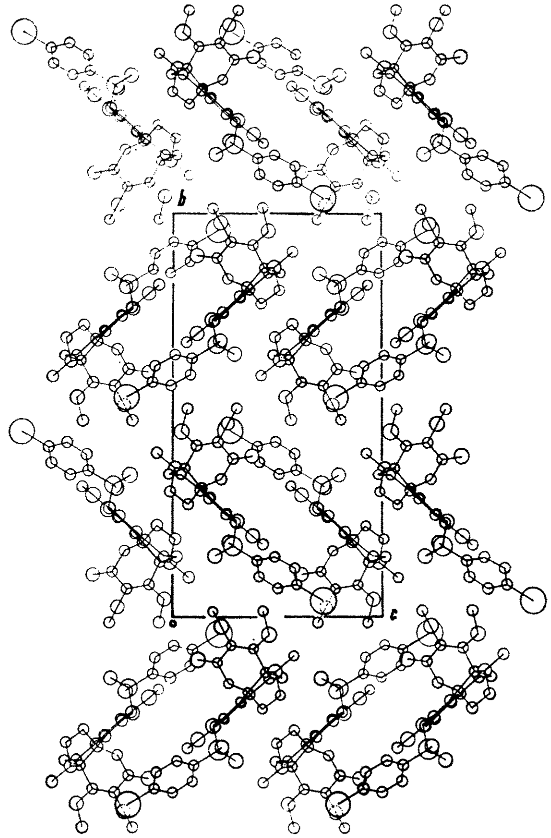
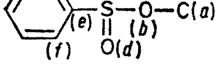


FIGURE 2 The arrangement of molecules in the crystal structure



(2)

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[7] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.

results shown in Table 4 for C–S–O–C torsion angles is consistent with Exner's deduction from dipole-moment measurements that there is only a small barrier to rotation about the S–OC bond in sulphonate esters.[8]

The mean C(sp^3)–O distance in the methoxy-groups in (1) is 1·47 Å whereas the mean C(sp^2)–O distance to these groups is 1·35 Å, indicative of some degree of double-bond character in the latter bonds. The C(sp^2)–O distance to the *p*-bromobenzenesulphonate group (1·42 Å) is significantly longer than the C(sp^2)–O distances to the methoxy-groups, and it is likely that the electronegative RSO_2 group restrains $O \rightarrow C(sp^2)$ donation of π electrons. It is, perhaps, pertinent that the carbon atom of the methoxy-group at C(3) is close to the plane of the aromatic ring whilst the sulphur atom is appreciably out of the plane [the C(3)–C(4)–O(3)–S torsion angle is 77°] and this distinction undoubtedly has a steric basis since an in-plane sulphur atom would be close to the oxygen substituent on C(3) or to a hydrogen substituent on C(5).

TABLE 4

Torsion angles (deg.) in various *p*-bromobenzenesulphonate groups (2): for convenience in comparing the magnitudes of the angles, signs have been omitted

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)
C(*g*)–C(*e*)–S–O(*c*)	11	10	7	6	12	24	3	25	22	23
C(*f*)–C(*e*)–S–O(*c*)	166	167	180	179	160	158	179	158	162	155
C(*g*)–C(*e*)–S–O(*d*)	144	141	129	138	141	157	135	161	154	155
C(*f*)–C(*e*)–S–O(*d*)	33	37	45	47	31	25	48	21	30	23
C(*g*)–C(*e*)–S–O(*b*)	105	105	115	111	103	92	113	88	95	91
C(*f*)–C(*e*)–S–O(*b*)	78	77	71	64	85	86	62	90	81	91
C(*a*)–O(*b*)–S–O(*c*)	5	0	151	50	67	46	64	28	59	38
C(*a*)–O(*b*)–S–O(*d*)	135	128	18	178	60	176	166	161	170	93
C(*a*)–O(*b*)–S–C(*e*)	113	116	95	66	176	69	52	83	56	154

(I) This work. (II) R. T. Puckett, G. A. Sim, A. D. Cross, and J. B. Siddall, *J. Chem. Soc.* (*B*), 1967, 783. (III) A. T. McPhail and G. A. Sim, *J. Chem. Soc.* (*B*), 1971, 198. (IV) A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc.* (*B*), 1968, 1249. (V) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1965, 1844. (VI) A. C. Macdonald and J. Trotter, *Acta Cryst.*, 1965, **18**, 243. (VII) T. Sato, M. Shiro, and H. Koyama, *J. Chem. Soc.* (*B*), 1968, 935. (VIII) B. E. Davidson and A. T. McPhail *J. Chem. Soc.* (*B*), 1970, 665. (IX) and (X) J. R. Hanson, G. M. McLaughlin, and G. A. Sim, *J.C.S. Perkin II*, 1972, 1124.

The mean C(sp^3)–N distance (1·48 Å) is close to the accepted value (*ca.* 1·47 Å).[9] The mean C(sp^3)–C(sp^3), C(sp^3)–C(sp^2), and aromatic C–C bond lengths (1·54, 1·50, and 1·41 Å) are in good agreement with expected values.

EXPERIMENTAL

Crystal Data.—$C_{26}H_{28}BrNO_7S$, $M = 578{\cdot}54$, Orthorhombic, $a = 8{\cdot}52$, $b = 24{\cdot}23$, $c = 12{\cdot}60$ Å, $U = 2601$ Å^3, $D_m = 1{\cdot}49$, $Z = 4$, $D_c = 1{\cdot}49$, $F(000) = 1192$. Space group $P2_12_12_1$ (D_2^4). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 34·8 cm^{-1}.

Crystallographic Measurements.—The cell dimensions were determined from precession photographs taken with Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). The diffraction intensities were recorded on equi-inclination multiple-film Weissenberg photographs of the *hk*0—11 layers, taken with Ni-filtered Cu-K_α radiation. Intensities of 1783 independent reflections above background were obtained by visual comparison with a set of calibrated intensities. Values of $|F_o|$ were derived by the usual mosaic-crystal formula.

Structure Analysis.—Preliminary co-ordinates of the bromine and sulphur atoms were deduced from a three-dimensional Patterson synthesis, and the positions of C(22) and C(25) obtained by interpolation. A weighted electron-density distribution[9] phased by these atoms (*R* 41%) yielded positions for all but one of the carbon, nitrogen, and oxygen atoms in the molecule. The missing atom was located in a subsequent electron-density map and structure (1; $R = O_2S{\cdot}C_6H_4Br$) established.

The approximate atomic parameters were adjusted by a series of least-squares calculations with a local version of the Gantzel, Sparks, and Trueblood UCLA full-matrix programme. The bromine and sulphur atoms were assigned anisotropic temperature factors but isotropic parameters were retained for the other atoms. The weighting scheme adopted was $\sqrt{w} = A/|F_o|$ for $|F_o| > A$ and $\sqrt{w} = 1$ for $|F_o| < A$, where $A = 0{\cdot}6\langle|F_o|\rangle$. Five rounds of calculations reduced *R* to 11·5%, and the refinement was then terminated.

To complete the analysis the effects of anomalous dispersion were allowed for, in order to determine the absolute stereochemistry of the alkaloid. Sets of structure factors were calculated with co-ordinates appropriate to (1) and to its mirror image, using values of $\Delta f'$ and $\Delta f''$ for bromine taken from ref. 10. The appropriate values of *R* were 11·3 and 11·5%, respectively, and Hamilton's test[11] indicates that this difference provides a significant demonstration of absolute configuration. Conversion of the alkaloid into hasubanonine provided an independent proof of the correctness of the absolute configuration.[2]

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[9] G. A. Sim, *Acta Cryst.*, 1959, **12**, 813; 1960, **13**, 511; 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon, Oxford, 1961, p. 227.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[11] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.