Molecular Conformations. Part XII.[1] Conformational Distortions in Tetracyclic Diterpenoids: *X*-Ray Diffraction Studies of the *p*-Bromobenzenesulphonyl Derivatives of Beyeran-3α-ol and 7β-Hydroxykaurenolide

By **J. R. Hanson**, **G. M. McLaughlin**, and **G. A. Sim**,*† School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The crystal structures of the *p*-bromobenzenesulphonyl derivatives of beyeran-3α-ol (3) and 7β-hydroxykaurenolide (4) have been elucidated by three-dimensional *X*-ray methods. In (3), rings A, B, and C have chair conformations, and a flexing of the perhydrophenanthrene skeleton so that the β-face is concave results in the C(20) · · · C(18) and C(20) · · · C(15) diaxial separations on the α-face of the molecule being 3·26 and 3·38 Å. In (4), on the other hand, ring A is very appreciably distorted from ideal chair geometry, with torsion angles which range from 33—67°, and rings B and C adopt distorted twisted boat conformations; these features are attributed to the γ-lactone which bridges rings A and B on the α-face and prevents an A,B,C-chair form of the molecule from flexing like (3) to relieve the C(20) · · · C(14) diaxial repulsion. The five-membered ring D approximates closely to an envelope form in (3) but is distorted towards a half-chair form in (4). The C(8)–C(14)–C(13) bridging valency angle in the bicyclo[3,2,1]octane moiety is substantially smaller than tetrahedral in both derivatives, 104° in (3) and 100° in (4). Both *p*-bromobenzenesulphonyl groups have conformations in which the S–OC bond is approximately perpendicular to the plane of the benzene ring; the S–O–C–H torsion angle is 9° in (3) and −22° in (4). Derivative (3) crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 12·454 ± 0·005, b = 27·734 ± 0·011, c = 7·308 ± 0·003 Å, and Z = 4. Derivative (4) crystallizes in the monoclinic space group $P2_1$ with a = 9·82, b = 11·45, c = 11·33 Å (all ±0·01 Å), β = 111° 40′ ± 20′, and Z = 2. The atomic co-ordinates were obtained by Fourier and least-squares calculations in which only the bromine atoms were assigned anisotropic thermal parameters, and the absolute configuration of each molecule was established by the anomalous-dispersion method. The final values of R are 10·2% over 2499 reflections (diffractometer) for (3) and 10·8% over 2222 reflections (photographic) for (4).

THE tetracyclic diterpenoids embrace a number of carbon skeletons, among which are the beyeranes (1) and kauranes (2).[2] The perhydrophenanthrene frameworks of these molecules have several pendent groups, and the consequent diaxial interactions can give rise to skeletal deformations from all-chair forms. In the beyerane

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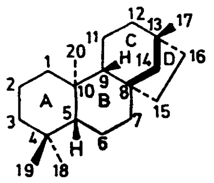
† *Present address:* Chemistry Department, University of Glasgow, Glasgow G12 8QQ.

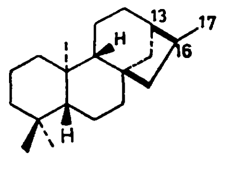
[1] Part XI, P. D. Cradwick and G. A. Sim, *J. Chem. Soc.* (*B*), 1971, 2218.

[2] J. R. Hanson, 'The Tetracyclic Diterpenes,' Pergamon, Oxford, 1968.

series the B/C ring junction is *trans* and the C(20)-methyl substituent at C(10) interacts with the C(15)–C(16) bridge, whilst in the kaurane series the ring junction is *cis* and the C(20)-methyl group interacts with the C(14)-methylene bridge. Moreover, in both series the C(20)-methyl group can interact with the C(18)-substituent on C(4) and with axial substituents at C(2) and C(6). Molecular models suggest that the rings A, B, and C may exist in a variety of chair, twisted boat, or boat forms with relief of various interactions, and these diterpenoids are therefore of considerable conformational interest.



(1)



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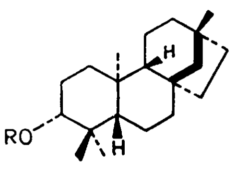
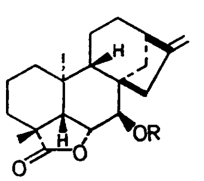


(3)



(4)

TABLE 1

Atomic co-ordinates (fractional) and temperature factors (Å^2), with standard deviations in parentheses, for (3)

	x	y	z	B
C(1)	0·2028(7)	0·3523(3)	0·2785(13)	3·87(17)
C(2)	0·3193(7)	0·3334(3)	0·2667(13)	3·80(18)
C(3)	0·3614(7)	0·3213(3)	0·4544(13)	3·54(16)
C(4)	0·3639(7)	0·3636(3)	0·5910(13)	3·75(17)
C(5)	0·2452(7)	0·3842(3)	0·5942(14)	3·53(16)
C(6)	0·2299(8)	0·4254(3)	0·7311(15)	4·37(20)
C(7)	0·1110(8)	0·4301(4)	0·7723(15)	4·63(21)
C(8)	0·0394(7)	0·4385(3)	0·6099(14)	3·75(17)
C(9)	0·0684(7)	0·4023(3)	0·4479(13)	3·46(16)
C(10)	0·1913(7)	0·3961(3)	0·4091(13)	3·28(15)
C(11)	0·0016(9)	0·4129(4)	0·2784(16)	4·84(21)
C(12)	−0·1178(10)	0·4194(4)	0·3211(18)	6·23(28)
C(13)	−0·1375(10)	0·4523(4)	0·4876(18)	6·09(27)
C(14)	−0·0797(9)	0·4313(4)	0·6520(16)	5·06(23)
C(15)	0·0354(8)	0·4926(4)	0·5413(16)	4·87(21)
C(16)	−0·0762(10)	0·4998(4)	0·4571(18)	5·82(25)
C(17)	−0·2598(12)	0·4574(5)	0·5175(21)	7·43(33)
C(18)	0·4497(9)	0·4007(4)	0·5348(17)	5·33(23)
C(19)	0·3915(9)	0·3438(4)	0·7779(16)	5·59(24)
C(20)	0·2411(8)	0·4410(3)	0·3099(14)	4·29(20)
C(21)	0·2568(9)	0·1787(4)	0·0723(17)	4·83(21)
C(22)	0·3561(10)	0·1939(4)	0·0067(16)	5·34(23)
C(23)	0·4277(9)	0·2138(4)	0·1261(17)	5·16(23)
C(24)	0·4036(8)	0·2180(4)	0·3072(14)	4·11(19)
C(25)	0·3040(8)	0·2024(4)	0·3737(16)	4·71(21)
C(26)	0·2320(9)	0·1829(4)	0·2550(17)	5·24(23)
O(1)	0·4712(5)	0·3021(2)	0·4284(10)	4·35(13)
O(2)	0·4667(6)	0·2331(3)	0·6390(11)	5·85(17)
O(3)	0·6013(6)	0·2399(3)	0·3920(12)	5·75(16)
S	0·4946(2)	0·2467(1)	0·4578(4)	4·39(5)
Br	0·1532(1)	0·1531(1)	−0·0931(2)	*

* The bromine atom was assigned an anisotropic temperature factor of the form: $T = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$ with parameters ($\times 10^4$):

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
101(1)	37(1)	372(4)	−6(1)	−17(2)	−28(1)

We have prepared the *p*-bromobenzenesulphonates of beyeran-3α-ol (3) and 7β-hydroxykaurenolide (4), and determined their molecular geometries by crystal-structure analysis. The kaurenolides have a lactone ring linking rings A and B and providing a mechanism for the relaying of distortions from one ring to the other.

TABLE 2

Interatomic distances (Å) for (3)

(*a*) Bond lengths

Br–C(21)	1·903(10)	C(8)–C(14)	1·522(14)
S–O(1)	1·579(7)	C(8)–C(15)	1·583(14)
S–O(2)	1·420(9)	C(9)–C(10)	1·561(12)
S–O(3)	1·421(8)	C(9)–C(11)	1·519(15)
S–C(24)	1·766(10)	C(10)–C(20)	1·567(13)
O(1)–C(3)	1·475(11)	C(11)–C(12)	1·525(17)
C(1)–C(2)	1·539(13)	C(12)–C(13)	1·539(18)
C(1)–C(10)	1·552(13)	C(13)–C(14)	1·516(17)
C(2)–C(3)	1·505(13)	C(13)–C(16)	1·538(17)
C(3)–C(4)	1·540(13)	C(13)–C(17)	1·540(20)
C(4)–C(5)	1·580(12)	C(15)–C(16)	1·528(16)
C(4)–C(18)	1·537(14)	C(21)–C(22)	1·388(16)
C(4)–C(19)	1·512(15)	C(21)–C(26)	1·375(17)
C(5)–C(6)	1·531(14)	C(22)–C(23)	1·361(16)
C(5)–C(10)	1·545(13)	C(23)–C(24)	1·362(16)
C(6)–C(7)	1·510(15)	C(24)–C(25)	1·396(14)
C(7)–C(8)	1·501(15)	C(25)–C(26)	1·358(16)
C(8)–C(9)	1·594(13)		

(*b*) Intramolecular non-bonded distances

C(19) · · · O(2)	3·364(13)	C(12) · · · C(15)	3·213(16)
C(18) · · · C(20)	3·264(15)	C(9) · · · C(16)	3·244(14)
C(15) · · · C(20)	3·380(14)	C(6) · · · C(20)	3·111(15)
C(18) · · · C(2)	3·154(14)	C(8) · · · C(20)	3·328(14)
C(18) · · · C(6)	3·156(15)	C(2) · · · C(20)	3·152(13)
C(5) · · · C(8)	2·968(12)	C(4) · · · C(20)	3·339(13)
C(5) · · · C(2)	2·925(13)	C(18) · · · C(2)	3·154(14)
C(18) · · · C(6)	3·156(15)	C(18) · · · C(10)	3·338(14)
C(11) · · · C(15)	2·960(15)	C(11) · · · C(16)	2·905(15)

(*c*) Intermolecular distances (<3·8 Å)

O(2) · · · C(22$^{\mathrm{I}}$)	3·21	O(3) · · · C(26$^{\mathrm{III}}$)	3·73
O(3) · · · C(25$^{\mathrm{III}}$)	3·44	O(3) · · · · C(1$^{\mathrm{III}}$)	3·73
O(1) · · · Br$^{\mathrm{IV}}$	3·56	O(3) · · · Br$^{\mathrm{IV}}$	3·74
O(2) · · · C(23$^{\mathrm{I}}$)	3·63	C(6) · · · C(20$^{\mathrm{II}}$)	3·77
C(19) · · · C(2$^{\mathrm{I}}$)	3·69		

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

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

The conformation of ring B of the kaurenolides has previously been examined by n.m.r. spectroscopy; the Karplus equation was applied to the coupling constants between the C(6) and C(7) protons for a series of 7-epimeric alcohols and their derivatives, and it was deduced that ring B exists in a twisted boat form.[3] The present *X*-ray results support and extend that conclusion.

The crystal structures of (3) and (4) (R = *p*-Br·C_6H_4·SO_2) were determined by Fourier and least-squares methods. Anisotropic thermal parameters were assigned to the bromine atoms, but the isotropic approximation was retained for the others, and at the end of the analyses *R* was 10·2% over 2499 independent reflections for compound (3) and 10·8% over 2222 independent reflections

[3] J. R. Hanson, *Tetrahedron*, 1966, **22**, 1701.

Table 3

Valency angles (deg.) for (3)

C(2)–C(1)–C(10)	112·8(7)	C(9)–C(10)–C(20)	112·5(7)
C(1)–C(2)–C(3)	110·5(8)	C(9)–C(11)–C(12)	112·7(9)
O(1)–C(3)–C(2)	106·5(7)	C(11)–C(12)–C(13)	112·7(1·0)
O(1)–C(3)–C(4)	109·8(7)	C(12)–C(13)–C(14)	108·9(1·0)
C(2)–C(3)–C(4)	115·3(7)	C(12)–C(13)–C(16)	108·3(1·0)
C(3)–C(4)–C(5)	105·5(7)	C(12)–C(13)–C(17)	108·9(1·1)
C(3)–C(4)–C(18)	110·6(8)	C(14)–C(13)–C(16)	102·1(1·0)
C(3)–C(4)–C(19)	108·3(8)	C(14)–C(13)–C(17)	112·9(1·1)
C(5)–C(4)–C(18)	114·1(7)	C(16)–C(13)–C(17)	115·4(1·0)
C(5)–C(4)–C(19)	109·2(8)	C(8)–C(14)–C(13)	104·4(9)
C(19)–C(4)–C(18)	109·1(8)	C(8)–C(15)–C(16)	106·2(8)
C(4)–C(5)–C(6)	113·3(8)	C(13)–C(16)–C(15)	106·2(9)
C(4)–C(5)–C(10)	117·9(8)	Br–C(21)–C(22)	119·6(9)
C(6)–C(5)–C(10)	111·0(7)	Br–C(21)–C(26)	119·8(8)
C(5)–C(6)–C(7)	108·4(8)	C(22)–C(21)–C(26)	120·5(1·1)
C(6)–C(7)–C(8)	115·7(9)	C(21)–C(22)–C(23)	118·8(1·1)
C(7)–C(8)–C(9)	110·8(7)	C(22)–C(23)–C(24)	120·9(1·0)
C(7)–C(8)–C(14)	113·2(9)	S–C(24)–C(23)	120·3(8)
C(7)–C(8)–C(15)	114·6(8)	S–C(24)–C(25)	119·2(8)
C(9)–C(8)–C(14)	106·6(8)	C(23)–C(24)–C(25)	120·4(1·0)
C(9)–C(8)–C(15)	111·7(8)	C(24)–C(25)–C(26)	118·9(1·0)
C(14)–C(8)–C(15)	99·2(8)	C(21)–C(26)–C(25)	120·5(1·1)
C(8)–C(9)–C(10)	115·1(7)	O(1)–S–O(2)	109·9(4)
C(8)–C(9)–C(11)	111·1(7)	O(1)–S–O(3)	104·7(4)
C(10)–C(9)–C(11)	113·9(8)	O(1)–S–C(24)	103·7(4)
C(1)–C(10)–C(5)	109·3(7)	O(2)–S–O(3)	120·6(5)
C(1)–C(10)–C(9)	106·8(7)	O(2)–S–C(24)	107·8(5)
C(1)–C(10)–C(20)	107·5(7)	O(3)–S–C(24)	109·0(5)
C(5)–C(10)–C(9)	106·7(7)	S–O(1)–C(3)	120·2(5)
C(5)–C(10)–C(20)	113·8(7)		

Table 4

Torsion angles (deg.) for (3). The angle *A*–*B*–*C*–*D* is defined as positive if, when viewed along the *B*–*C* bond, atom *A* must be rotated clockwise to eclipse atom *D*. The standard deviations of the angles are *ca.* 1°

C(10)–C(1)–C(2)–C(3)	56	C(14)–C(8)–C(15)–C(16)	29
C(2)–C(1)–C(10)–C(5)	−50	C(8)–C(9)–C(10)–C(1)	168
C(2)–C(1)–C(10)–C(9)	−165	C(8)–C(9)–C(10)–C(5)	52
C(2)–C(1)–C(10)–C(20)	74	C(8)–C(9)–C(10)–C(20)	−74
C(1)–C(2)–C(3)–O(1)	178	C(11)–C(9)–C(10)–C(1)	−62
C(1)–C(2)–C(3)–C(4)	−60	C(11)–C(9)–C(10)–C(5)	−178
O(1)–C(3)–C(4)–C(5)	175	C(11)–C(9)–C(10)–C(20)	56
O(1)–C(3)–C(4)–C(18)	51	C(8)–C(9)–C(11)–C(12)	−47
O(1)–C(3)–C(4)–C(19)	−68	C(10)–C(9)–C(11)–C(12)	−179
C(2)–C(3)–C(4)–C(5)	55	C(9)–C(11)–C(12)–C(13)	46
C(2)–C(3)–C(4)–C(18)	−69	C(11)–C(12)–C(13)–C(14)	−57
C(2)–C(3)–C(4)–C(19)	171	C(11)–C(12)–C(13)–C(16)	53
C(3)–C(4)–C(5)–C(6)	177	C(11)–C(12)–C(13)–C(17)	179
C(3)–C(4)–C(5)–C(10)	−51	C(12)–C(13)–C(14)–C(8)	70
C(18)–C(4)–C(5)–C(6)	−61	C(16)–C(13)–C(14)–C(8)	−44
C(18)–C(4)–C(5)–C(10)	71	C(17)–C(13)–C(14)–C(8)	−169
C(19)–C(4)–C(5)–C(6)	61	C(12)–C(13)–C(16)–C(15)	−90
C(19)–C(4)–C(5)–C(10)	−167	C(14)–C(13)–C(16)–C(15)	24
C(4)–C(5)–C(6)–C(7)	−160	C(17)–C(13)–C(16)–C(15)	147
C(10)–C(5)–C(6)–C(7)	65	C(8)–C(15)–C(16)–C(13)	4
C(4)–C(5)–C(10)–C(1)	50	Br–C(21)–C(22)–C(23)	178
C(4)–C(5)–C(10)–C(9)	165	C(26)–C(21)–C(22)–C(23)	−1
C(4)–C(5)–C(10)–C(20)	−70	Br–C(21)–C(26)–C(25)	−178
C(6)–C(5)–C(10)–C(1)	−177	C(22)–C(21)–C(26)–C(25)	1
C(6)–C(5)–C(10)–C(9)	−62	C(21)–C(22)–C(23)–C(24)	1
C(6)–C(5)–C(10)–C(20)	63	C(22)–C(23)–C(24)–S	−177
C(5)–C(6)–C(7)–C(8)	−57	C(22)–C(23)–C(24)–C(25)	−1
C(6)–C(7)–C(8)–C(9)	47	S–C(24)–C(25)–C(26)	176
C(6)–C(7)–C(8)–C(14)	167	C(23)–C(24)–C(25)–C(26)	0
C(6)–C(7)–C(8)–C(15)	−81	C(24)–C(25)–C(26)–C(21)	0
C(7)–C(8)–C(9)–C(10)	−45	O(2)–S–O(1)–C(3)	−59
C(7)–C(8)–C(9)–C(11)	−176	O(3)–S–O(1)–C(3)	170
C(14)–C(8)–C(9)–C(10)	−168	C(24)–S–O(1)–C(3)	56
C(14)–C(8)–C(9)–C(11)	60	O(1)–S–C(24)–C(23)	81
C(15)–C(8)–C(9)–C(10)	84	O(1)–S–C(24)–C(25)	−95
C(15)–C(8)–C(9)–C(11)	−47	O(2)–S–C(24)–C(23)	−162
C(7)–C(8)–C(14)–C(13)	168	O(2)–S–C(24)–C(25)	22
C(9)–C(8)–C(14)–C(13)	−70	O(3)–S–C(24)–C(23)	−30
C(15)–C(8)–C(14)–C(13)	46	O(3)–S–C(24)–C(25)	154
C(7)–C(8)–C(15)–C(16)	−150	S–O(1)–C(3)–C(2)	−108
C(9)–C(8)–C(15) C(16)	83	S–O(1)–C(3)–C(4)	126

for compound (4). The final atomic co-ordinates and molecular dimensions for compound (3) are listed in Tables 1—5, and the corresponding results for compound (4) are in Tables 6—10. Views of the molecular structures are shown in Figures 1 and 2.

Table 5

Displacements (Å) of the atoms from various planes in compound (3)

Plane (*a*): C(2), C(3), C(5), C(10)

C(2) −0·027, C(3) 0·028, C(5) −0·028, C(10) 0·027, C(1) 0·639, C(4) −0·672

Plane (*b*): C(5), C(7), C(8), C(10)

C(5) 0·054, C(7) −0·056, C(8) 0·052, C(10) −0·050, C(6) −0·717, C(9) 0·599

Plane (*c*): C(8), C(9), C(12), C(13)

C(8) −0·012, C(9) 0·011, C(12) −0·012, C(13) 0·013, C(11) −0·569, C(14) 0·835

Plane (*d*): C(8), C(13), C(15), C(16)

C(8) 0·013, C(13) −0·014, C(15) −0·021, C(16) 0·021, C(14) −0·676

Plane (*e*): C(6), C (8), C(10)

C(6) 0, C(8) 0, C(10) 0, C(1) 0·697, C(2) 0·738, C(3) 1·392, C(4) 0·701, C(5) 0·603, C(7) 0·397, C(9) 0·367, C(11) −0·119, C(12) 0·239, C(13) −0·065, C(14) 0·695

Table 6

Atomic co-ordinates (fractional) and temperature factors (Å^2), with standard deviations in parentheses, for (4)

	x	*y*	*z*	*B*
C(1)	0·8113(16)	−0·3669(15)	0·7920(14)	2·51(26)
C(2)	0·8087(17)	−0·4374(16)	0·6738(15)	2·76(28)
C(3)	0·7539(16)	−0·3607(16)	0·5559(14)	2·56(27)
C(4)	0·6250(15)	−0·2782(14)	0·5428(13)	2·32(26)
C(5)	0·6215(13)	−0·2292(13)	0·6683(11)	1·53(21)
C(6)	0·4642(14)	−0·1871(14)	0·6284(12)	1·77(22)
C(7)	0·4072(14)	−0·1917(14)	0·7344(12)	1·76(22)
C(8)	0·5219(14)	−0·1691(13)	0·8646(12)	1·70(22)
C(9)	0·6606(13)	−0·2491(16)	0·8927(11)	1·94(21)
C(10)	0·6586(14)	−0·3204(13)	0·7756(12)	1·75(22)
C(11)	0·6886(19)	−0·3242(17)	1·0120(16)	3·31(32)
C(12)	0·7037(18)	−0·2471(23)	1·1289(16)	3·69(32)
C(13)	0·5933(16)	−0·1470(16)	1·0889(14)	2·64(26)
C(14)	0·4576(15)	−0·1843(15)	0·9682(13)	2·19(25)
C(15)	0·5755(16)	−0·0401(15)	0·8883(14)	2·28(25)
C(16)	0·6515(17)	−0·0449(17)	1·0362(15)	2·65(27)
C(17)	0·7546(20)	0·0319(19)	1·1113(18)	3·79(36)
C(18)	0·4711(16)	−0·3281(16)	0·4847(15)	2·66(27)
C(19)	0·6323(22)	−0·1751(20)	0·4548(19)	4·24(39)
C(20)	0·5580(16)	−0·4282(16)	0·7538(14)	2·47(27)
C(21)	−0·0887(17)	0·1303(16)	0·7945(15)	2·75(29)
C(22)	−0·0663(17)	0·1579(16)	0·6843(14)	2·66(28)
C(23)	−0·0020(17)	0·0744(16)	0·6348(15)	2·73(28)
C(24)	0·0426(15)	−0·0321(15)	0·7032(13)	2·03(24)
C(25)	0·0152(16)	−0·0536(15)	0·8147(14)	2·38(26)
C(26)	−0·0513(17)	0·0271(16)	0·8592(14)	2·59(28)
O(1)	0·2937(10)	−0·1014(9)	0·7116(9)	2·21(17)
O(2)	0·0836(13)	−0·1188(13)	0·5066(12)	4·02(25)
O(3)	0·1063(12)	−0·2519(15)	0·6860(10)	3·82(22)
O(4)	0·4293(13)	−0·4052(12)	0·4040(11)	3·76(24)
O(5)	0·3790(11)	−0·2699(11)	0·5269(9)	2·88(20)
S	0·1268(4)	−0·1388(4)	0·6420(4)	2·37(7)
Br	−0·1738(2)	0·2500(—)	0·8613(2)	*

* The bromine atom was assigned an anisotropic temperature factor of the form: $T = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$ with parameters ($\times 10^4$):

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
162(3)	84(4)	112(2)	41(2)	59(2)	−21(2)

Rings A, B, and C of the beyerane derivative (3) have chair conformations. The internal torsion angles range from 50—60° in ring A, 45—65° in ring B, and 46—70° in ring C, indicating that the deviations from ideal chair geometry increase in the order A < B < C. Atoms C(4) and C(2) of ring A are appreciably (0·70 and 0·74 Å) above the plane defined by atoms C(6), C(8), and C(10) of ring B, whereas atoms C(11) and C(13) of ring C are very slightly (0·12 and 0·06 Å) below the plane; all these atoms would be coplanar in an ideal perhydrophenanthrene system and the displacements demonstrate that the skeleton of (3) is bowed so as to be concave on the β-face. This distortion relieves the repulsive axial interactions on the α-face of the molecule, and the C(20) ··· C(18) and C(20) ··· C(15) separations are 3·26 and 3·38 Å.

TABLE 7

Interatomic distances (Å) for (4)

(*a*) Bond lengths

Br–C(21)	1·928(19)	C(7)–C(8)	1·511(16)
S–O(1)	1·592(10)	C(8)–C(9)	1·573(20)
S–O(2)	1·452(13)	C(8)–C(14)	1·535(23)
S–O(3)	1·428(18)	C(8)–C(15)	1·557(23)
S–C(24)	1·754(18)	C(9)–C(10)	1·552(21)
O(1)–C(7)	1·471(18)	C(9)–C(11)	1·538(24)
O(4)–C(18)	1·227(21)	C(10)–C(20)	1·542(22)
O(5)–C(6)	1·487(17)	C(11)–C(12)	1·553(28)
O(5)–C(18)	1·346(22)	C(12)–C(13)	1·527(28)
C(1)–C(2)	1·556(25)	C(13)–C(14)	1·575(18)
C(1)–C(10)	1·537(22)	C(13)–C(16)	1·516(27)
C(2)–C(3)	1·521(23)	C(15)–C(16)	1·564(20)
C(3)–C(4)	1·542(23)	C(16)–C(17)	1·373(24)
C(4)–C(5)	1·541(21)	C(21)–C(22)	1·383(26)
C(4)–C(18)	1·519(20)	C(21)–C(26)	1·366(24)
C(4)–C(19)	1·564(29)	C(22)–C(23)	1·374(27)
C(5)–C(6)	1·518(18)	C(23)–C(24)	1·425(24)
C(5)–C(10)	1·540(19)	C(24)–C(25)	1·406(24)
C(6)–C(7)	1·501(22)	C(25)–C(26)	1·333(26)

(*b*) Intramolecular non-bonded distances

C(18) ··· C(20)	3·068(23)	C(20) ··· O(5)	3·105(18)
C(18) ··· C(2)	3·449(20)	C(9) ··· C(16)	2·868(26)
C(18) ··· C(10)	3·127(18)	C(12) ··· C(15)	3·478(26)
C(20) ··· C(2)	2·923(26)	C(11) ··· C(14)	2·669(24)
C(20) ··· C(6)	3·085(23)	C(9) ··· C(13)	2·798(24)
C(20) ··· C(4)	3·203(24)	C(8) ··· C(12)	3·002(20)
C(20) ··· C(11)	2·975(23)	C(7) ··· C(10)	2·761(20)
C(20) ··· O(4)	3·698(19)	C(6) ··· C(9)	2·988(16)
C(20) ··· C(8)	3·290(23)	C(5) ··· C(8)	2·825(21)

(*c*) Intermolecular distances (<3·7 Å)

C(22) ··· O(5^{IV})	3·23	O(2) ··· C(3^{III})	3·55
C(21) ··· O(4^{IV})	3·29	C(2) ··· O(3^{I})	3·57
C(22) ··· O(2^{IV})	3·31	C(22) ··· C(12^{II})	3·57
C(17) ··· O(3^{II})	3·31	Br ··· O(4^{IV})	3·58
O(2) ··· C(2^{III})	3·35	C(20) ··· O(4^{III})	3·63
C(22) ··· O(4^{IV})	3·40	C(15) ··· O(4^{III})	3·64
C(3) ··· O(3^{I})	3·45	C(13) ··· C(20^{II})	3·69
C(6) ··· O(4^{III})	3·45		

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

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

Ring C constitutes part of a bicyclo[3,2,1]octane system and the displacements of atoms C(11) and C(14) from the mean plane through atoms C(8), C(9), C(12), and C(13) in compound (3) are —0·57 and 0·84 Å. The displacements are similar to those in a variety of other bicyclo[3,2,1]octanes in which the six-membered ring adopts the chair form,[4] and may be compared with the value of 0·73 Å appropriate to an ideal cyclohexane ring. The flattening of ring C at position 11 and the additional puckering at position 14 are also evident in the ring torsion angles which are *ca.* 70° for bonds C(8)–C(14) and C(13)–C(14), *ca.* 59° for C(8)–C(9) and C(12)–C(13), and *ca.* 46° for C(9)–C(11) and C(12)–C(11). This pattern is similar to, though more extreme than, that found in twin-chair bicyclo[3,3,1]nonanes, where the corresponding angles are typically *ca.* 63, 55, and 45°.[1] From n.m.r. measurements, Jefford *et al.*[5] have estimated that the angle ϕ_{ea} between equatorial and axial protons at positions 2 and 3 in bicyclo[3,2,1]octan-3-ol is 44°; this angle should, and does, differ only trivially from the C(8)–C(9)–C(11)–C(12) and C(13)–C(12)–C(11)–C(9) torsion angles in compound (3). The C(3) ··· C(6) and C(3) ··· C(7) distances in bicyclo[3,2,1]octane have been estimated on the basis of strain-energy calculations to be 2·94 Å,[6] and the appropriate C(11) ··· C(15) and C(11) ··· C(16) distances in (3) are 2·96 and 2·91 Å.

TABLE 8

Valency angles (deg.) for (4)

C(2)–C(1)–C(10)	111·8(1·1)	C(9)–C(10)–C(20)	111·3(1·3)
C(1)–C(2)–C(3)	110·1(1·5)	C(9)–C(11)–C(12)	111·2(1·6)
C(2)–C(3)–C(4)	116·7(1·5)	C(11)–C(12)–C(13)	109·8(1·2)
C(3)–C(4)–C(5)	115·6(1·0)	C(12)–C(13)–C(14)	109·6(1·4)
C(3)–C(4)–C(18)	117·5(1·4)	C(12)–C(13)–C(16)	111·5(1·5)
C(3)–C(4)–C(19)	107·1(1·5)	C(14)–C(13)–C(16)	100·8(1·2)
C(5)–C(4)–C(18)	100·3(1·3)	C(8)–C(14)–C(13)	100·3(1·2)
C(5)–C(4)–C(19)	109·6(1·4)	C(8)–C(15)–C(16)	98·6(1·3)
C(18)–C(4)–C(19)	106·3(1·2)	C(13)–C(16)–C(15)	110·4(1·3)
C(4)–C(5)–C(6)	102·0(9)	C(13)–C(16)–C(17)	123·3(1·5)
C(4)–C(5)–C(10)	113·7(1·2)	C(15)–C(16)–C(17)	126·4(1·7)
C(6)–C(5)–C(10)	111·6(1·2)	O(4)–C(18)–O(5)	122·5(1·4)
O(5)–C(6)–C(5)	104·4(1·2)	O(4)–C(18)–C(4)	126·8(1·7)
O(5)–C(6)–C(7)	109·1(1·2)	O(5)–C(18)–C(4)	110·5(1·3)
C(5)–C(6)–C(7)	112·9(1·0)	Br–C(21)–C(22)	116·1(1·3)
O(1)–C(7)–C(6)	108·5(1·1)	Br–C(21)–C(26)	118·4(1·4)
O(1)–C(7)–C(8)	107·1(1·2)	C(22)–C(21)–C(26)	125·5(1·8)
C(6)–C(7)–C(8)	114·3(1·2)	C(21)–C(22)–C(23)	117·4(1·6)
C(7)–C(8)–C(9)	112·1(1·2)	C(22)–C(23)–C(24)	118·0(1·6)
C(7)–C(8)–C(14)	111·0(1·1)	S–C(24)–C(23)	118·4(1·3)
C(7)–C(8)–C(15)	114·4(1·1)	S–C(24)–C(25)	120·5(1·2)
C(9)–C(8)–C(14)	110·4(1·1)	C(23)–C(24)–C(25)	121·0(1·6)
C(9)–C(8)–C(15)	107·8(1·1)	C(24)–C(25)–C(26)	120·1(1·6)
C(14)–C(8)–C(15)	100·6(1·1)	C(21)–C(26)–C(25)	117·9(1·7)
C(8)–C(9)–C(10)	113·3(1·0)	O(1)–S–O(2)	109·1(7)
C(8)–C(9)–C(11)	111·4(1·3)	O(1)–S–O(3)	108·8(6)
C(10)–C(9)–C(11)	113·5(1·5)	O(1)–S–C(24)	99·6(6)
C(1)–C(10)–C(5)	105·4(1·3)	O(2)–S–O(3)	119·2(8)
C(1)–C(10)–C(9)	112·0(1·0)	O(2)–S–C(24)	108·2(8)
C(1)–C(10)–C(20)	106·3(1·3)	O(3)–S–C(24)	110·2(9)
C(5)–C(10)–C(9)	104·1(1·2)	S–O(1)–C(7)	118·2(9)
C(5)–C(10)–C(20)	117·7(1·0)	C(6)–O(5)–C(18)	109·3(1·1)

Ring D of compound (3) approximates closely to an envelope conformation, with C(14) displaced by 0·68 Å from the mean plane through atoms C(8), C(13), C(15), and C(16). The five-membered ring of the bicyclo[3,2,1]octane fragment in methyl gibberellate di-*p*-bromobenzoate [7] and the five-membered ring in pseudotropine [8] exhibit envelope conformations in the crystals,

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[6] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582.

[7] J. A. Hartsuck and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1963, **85**, 3414.

[8] H. Schenk, C. H. MacGillavry, S. Skolnik, and J. Laan, *Acta Cryst.*, 1967, **23**, 423.

TABLE 9

Torsion angles (deg) for (4) defined as for Table 4. The standard deviations of the angles are *ca.* 2°

C(10)–C(1)–C(2)–C(3)	59	C(15)–C(8)–C(14)–C(13)	−54
C(2)–C(1)–C(10)–C(5)	−67	C(7)–C(8)–C(15)–C(16)	164
C(2)–C(1)–C(10)–C(9)	−180	C(9)–C(8)–C(15)–C(16)	−70
C(2)–C(1)–C(10)–C(20)	59	C(14)–C(8)–C(15)–C(16)	45
C(1)–C(2)–C(3)–C(4)	−40	C(8)–C(9)–C(10)–C(1)	162
C(2)–C(3)–C(4)–C(5)	33	C(8)–C(9)–C(10)–C(5)	49
C(2)–C(3)–C(4)–C(18)	−85	C(8)–C(9)–C(10)–C(20)	−79
C(2)–C(3)–C(4)–C(19)	156	C(11)–C(9)–C(10)–C(1)	−69
C(3)–C(4)–C(5)–C(6)	−163	C(11)–C(9)–C(10)–C(5)	177
C(3)–C(4)–C(5)–C(10)	−42	C(11)–C(9)–C(10)–C(20)	49
C(18)–C(4)–C(5)–C(6)	−35	C(8)–C(9)–C(11)–C(12)	−56
C(18)–C(4)–C(5)–C(10)	85	C(10)–C(9)–C(11)–C(12)	175
C(19)–C(4)–C(5)–C(6)	76	C(9)–C(11)–C(12)–C(13)	39
C(19)–C(4)–C(5)–C(10)	−163	C(11)–C(12)–C(13)–C(14)	27
C(3)–C(4)–C(18)–O(4)	−31	C(11)–C(12)–C(13)–C(16)	−84
C(3)–C(4)–C(18)–O(5)	153	C(12)–C(13)–C(14)–C(8)	−78
C(5)–C(4)–C(18)–O(4)	−157	C(16)–C(13)–C(14)–C(8)	40
C(5)–C(4)–C(18)–O(5)	27	C(12)–C(13)–C(16)–C(15)	105
C(19)–C(4)–C(18)–O(4)	89	C(12)–C(13)–C(16)–C(17)	−76
C(19)–C(4)–C(18)–O(5)	−87	C(14)–C(13)–C(16)–C(15)	−11
C(4)–C(5)–C(6)–O(5)	32	C(14)–C(13)–C(16)–C(17)	168
C(4)–C(5)–C(6)–C(7)	151	C(8)–C(15)–C(16)–C(13)	−21
C(10)–C(5)–C(6)–O(5)	−89	C(8)–C(15)–C(16)–C(17)	160
C(10–C(5)–C(6)–C(7)	29	Br–C(21)–C(22)–C(23)	180
C(4)–C(5)–C(10)–C(1)	57	C(26)–C(21)–C(22)–C(23)	1
C(4)–C(5)–C(10)–C(9)	176	Br–C(21)–C(26)–C(25)	−178
C(4)–C(5)–C(10)–C(20)	−61	C(22)–C(21)–C(26)–C(25)	1
C(6)–C(5)–C(10)–C(1)	172	C(21)–C(22)–C(23)–C(24)	−3
C(6)–C(5)–C(10)–C(9)	−70	C(22)–C(23)–C(24)–S	−179
C(6)–C(5)–C(10)–C(20)	54	C(22)–C(23)–C(24)–C(25)	3
O(5)–C(6)–C(7)–O(1)	−92	S–C(24)–C(35)–C(26)	−179
O(5)–C(6)–C(7)–C(8)	148	C(23)–C(24)–C(25)–C(26)	−1
C(5)–C(6)–C(7)–O(1)	152	C(24)–C(25)–C(26)–C(21)	−1
C(5)–C(6)–C(7)–C(8)	33	O(2)–S–O(1)–C(7)	−93
O(1)–C(7)–C(8)–C(9)	−172	O(3)–S–O(1)–C(7)	38
O(1)–C(7)–C(8)–C(14)	64	C(24)–S–O(1)–C(7)	154
O(1)–C(7)–C(8)–C(15)	−49	O(1)–S–C(24)–C(23)	91
C(6)–C(7)–C(8)–C(9)	−52	O(1)–S–C(24)–C(25)	−91
C(6)–C(7)–C(8)–C(14)	−176	O(2)–S–C(24)–C(23)	−23
C(6)–C(7)–C(8)–C(15)	71	O(2)–S–C(24)–C(25)	155
C(7)–C(8)–C(9)–C(10)	8	O(3)–S–C(24)–C(23)	−155
C(7)–C(8)–C(9)–C(11)	−122	O(3)–S–C(24)–C(25)	23
C(14)–C(8)–C(9)–C(10)	132	S–O(1)–C(7)–C(6)	96
C(14)–C(8)–C(9)–C(11)	3	S–O(1)–C(7)–C(8)	−140
C(15)–C(8)–C(9)–C(10)	−119	C(18)–O(5)–C(6)–C(7)	−137
C(15)–C(8)–C(9)–C(11)	112	C(6)–O(5)–C(18)–O(4)	177
C(7)–C(8)–C(14)–C(13)	−176	C(6)–O(5)–C(18)–C(4)	−7
C(9)–C(8)–C(14)–C(13)	59	C(18)–O(5)–C(6)–C(5)	−17

TABLE 10

Displacements (Å) of atoms from various planes in compound (4)

Plane (*a*): C(2), C(3), C(5), C(10)

C(2) −0·059, C(3) 0·058, C(5) −0·057, C(10) 0·058, C(1) −0·737, C(4) 0·457

Plane (*b*): C(5), C(6), C(8), C(9)

C(5) −0·119, C(6) 0·114, C(8) −0·110, C(9) 0·114, C(7) 0·510, C(10) 0·741

Plane (*c*): C(8), C(9), C(12), C(13)

C(8) −0·097, C(9) −0·090, C(12) 0·094, C(13) −0·100, C(14) 0·863, C(11) 0·602

Plane (*d*): C(13), C(15)—(17)

C(13) 0·002, C(15) 0·002, C(16) −0·006, C(17) 0·002, C(14) 0·321, C(8) −0·530

Plane (*e*): O(4), O(5), C(4), C(6), C(18)

O(4) 0·019, O(5) −0·050, C(4) −0·023, C(6) 0·037, C(18) 0·017, C(5) 0·580

but the five-membered rings in a number of 6- and 6,7-substituted bicyclo[3,2,1]octanes are closer to half-chair forms, and in an enmein derivative, for example, the C(5)–C(6)–C(7)–C(1) torsion angle of the bicyclo-octane is 14°.[4] The five-membered rings in 2- and 2,3-substituted bicyclo[2,2,1]heptanes are normally slightly twisted away from ideal envelope forms,[9] though the deviations are appreciably smaller than those in the bicyclo[3,2,1]octanes.

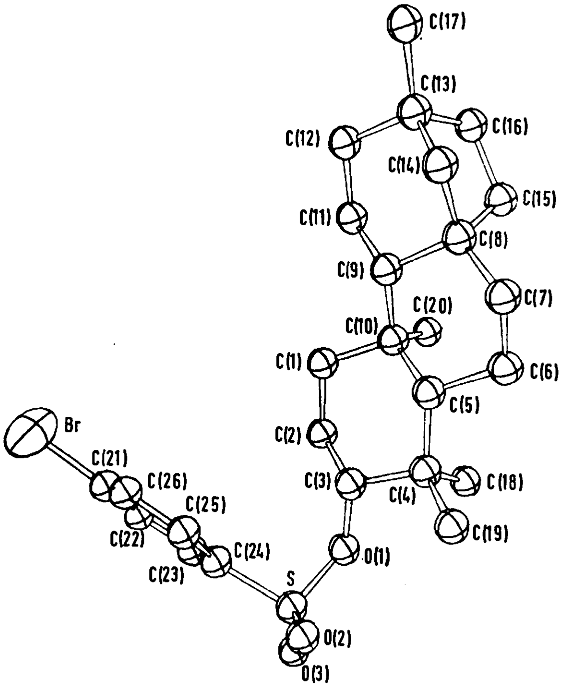

FIGURE 1 The molecular structure of (3)

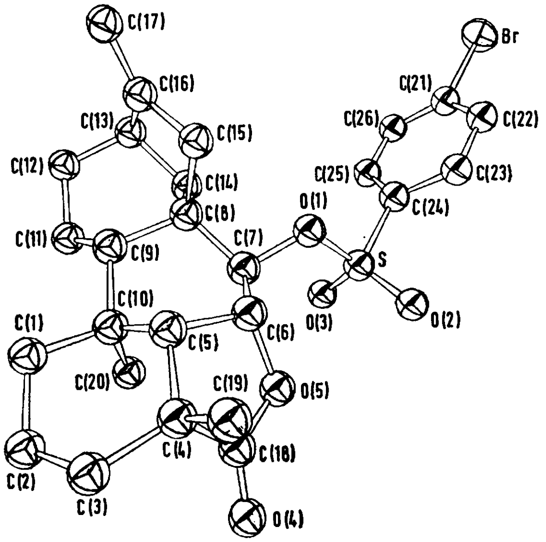

FIGURE 2 The molecular structure of (4)

Though ring A of the kaurenolide derivative (4) has a very distorted chair conformation, rings B and C have

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[9] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995.

twisted boat conformations. The contrast with the beyerane derivative (3) arises because the γ-lactone which bridges rings A and B on the α-face of (4) prevents an A,B,C-chair form of the molecule from flexing like (3) to relieve C(20) · · · C(14) and C(20) · · · C(19) diaxial repulsions. The C(2)–C(3)–C(4)–C(5) torsion angle in ring A has the remarkably small value of 33°, and C(2)–C(1)–C(10)–C(5), the opposite angle in the ring, is −67°; the other angles have intermediate magnitudes (see Table 4). In rings B and C the torsion angles about bond C(8)–C(9) (8° in ring B and 3° in ring C) are close to 0°. Since the opposite torsion angles in these rings, C(10)–C(5)–C(6)–C(7) in ring B and C(11)–C(12)–C(13)–C(14) in ring C, are respectively 29 and 27°, the conformations of these rings are considerably distorted from classical boat forms. The skewing of the rings is also evident in the displacements by $\pm 0{\cdot}1$ Å of atoms C(5), C(6), C(8), and C(9) in ring B and of atoms C(8), C(9), C(12), and C(13) in ring C from the mean planes through these sets of atoms.

Ring D adopts a conformation intermediate between envelope and half-chair forms. Atoms C(13), C(15), C(16), and C(17) are closely coplanar, and C(8) and C(14) are displaced by 0·32 and −0·53 Å from the plane. The C(8)–C(15)–C(16)–C(13) torsion angle is −21°, whereas in an ideal envelope form of ring D this angle would be 0° [*cf.* 4° in the beyerane derivative (3)]. In the lactone ring the C(6)–O(5)–C(18)–C(4) torsion angle is −7°, and the ring therefore departs slightly from the ideal envelope form.

In a n.m.r. study of various kaurenolides and related molecules, Hanson deduced that $\phi_{6\beta,7\alpha}$, the dihedral angle between the 6β and 7α protons, is *ca.* 140° and that $\phi_{5\beta,6\beta}$ is *ca.* 39°.[3] From the torsion angles derived for compound (4) in the solid state, we deduce that $\phi_{6\beta,7\alpha}$ is 150° and $\phi_{5\beta,6\beta}$ is 31°. The good agreement with the n.m.r. results strongly supports the hypothesis that the conformation does not alter significantly between solution and the solid state.

The *p*-bromobenzenesulphonyl group normally adopts a conformation in which the S–OR bond is steeply inclined to the benzene plane.[10] The beyerane and kaurenolide derivatives adhere to this pattern, the torsion angle C(23)–C(24)–S–O(1) being 81° in (3) and 91° in (4). The conformation of the sulphonate ester is also partially characterized by the C–S–O–C torsion angle, which is 56° in (3) and 154° in (4); in vernolepin *p*-bromobenzenesulphonate the C–S–O–C torsion angle is 95°,[10] and these diverse results are consistent with Exner's deduction that there is only a small barrier to rotation about the S–OR bond in sulphonates.[11] The orientation of the O(1)–S bond in relation to the cyclohexane ring can be defined by the torsion angle H–C–O–S, which is *ca.* 9° in (3) and *ca.* −22° in (4). The mean dimensions of the *p*-bromobenzenesulphonyl residues in (3) and (4) (C–S=O 109, C–S–O 102, O=S=O 120, O–S=O 108, and S–O–C 119°; S=O 1·43, S–O 1·59, C–S 1·76, C–Br 1·92, and O–C 1·48 Å) are in excellent agreement with the mean values in seven other compounds.[12]

The C(sp^3)–C(sp^3) bonds in compound (3) range in length from 1·501 to 1·594 Å, mean 1·539 Å. Some of the variations appear to be genuine and suggest that steric effects are involved, for the mean of the five bonds having only one hydrogen substituent on the carbon atoms is 1·564 Å, that of the seven with two hydrogen atoms is 1·539 Å, of the seven with three hydrogen atoms 1·529 Å, and of the four with four hydrogen atoms 1·526 Å. Similar trends have been noted for other molecules.[13] The standard deviations of the bond lengths in compound (4) are appreciably larger, and the pattern is obscured in this case.

EXPERIMENTAL

(*a*) *Compound* (3)

Crystal Data.—$C_{26}H_{37}BrO_3S$, $M = 509{\cdot}6$. Orthorhombic, $a = 12{\cdot}454 \pm 0{\cdot}005$, $b = 27{\cdot}734 \pm 0{\cdot}011$, $c = 7{\cdot}308 \pm 0{\cdot}003$ Å, $U = 2524$ Å^3, $D_m = 1{\cdot}34$, $Z = 4$, $D_c = 1{\cdot}34$, $F(000) = 1072$. Space group $P2_12_12_1$ (D_2^4). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 18·3 cm^{-1}.

Crystallographic Measurements.—Preliminary values of the cell dimensions were obtained from precession photographs, and were subsequently adjusted by a least-squares treatment of the θ, χ, and ϕ setting angles of twelve reflections measured with zirconium-filtered Mo-K_α radiation on a Hilger and Watts' Y 290 automatic diffractometer. Intensity data were collected by the θ—2θ step scan procedure, each reflection being scanned in 40 equal steps of 0·02° from 0·4° below to 0·4° above $2\theta_{\text{calc}}$. The intensities of two standard reflections were monitored periodically and the results used to ensure that all reflections were on a common scale; however, the changes in the standard reflections during data collection were small, and there was no evidence of crystal deterioration. Intensities were collected for reflections within θ(Mo-K_α) < 30°, and 2499 reflections for which $I \geqslant 2{\cdot}8\sigma(I)$ were accepted as being significantly above background and were corrected for Lorentz-polarization effects. Absorption was neglected.

Structure Analysis.—Approximate co-ordinates of the bromine atom were derived from a three-dimensional Patterson synthesis, and the positions of the sulphur, carbon, and oxygen atoms obtained from two subsequent electron-density distributions.

The approximate atomic parameters were adjusted by a series of full-matrix least-squares calculations using the ORFLS programme in the '*X*-Ray '63' system.[14] Several cycles of calculations with isotropic thermal parameters reduced *R* to 17·0%, at which stage the bromine atom was assigned an anisotropic temperature factor and further refinement then gave *R* 12·9%. Dispersion corrections were then incorporated in the least-squares programme for the bromine atom, and when structure factors were calculated on the basis of the two alternative absolute configurations the stereochemistry shown in (3) gave *R* 12·4%, whereas the

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[13] S. R. Hall and E. N. Maslen, *Acta Cryst.*, 1965, **18**, 265; K. W. Muir and G. A. Sim, *J. Chem. Soc.* (*B*), 1968, 667.

[14] '*X*-Ray '63,' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

mirror image gave R 13·8%; this result is in accord with the established absolute configuration of beyerane derivatives.[2] A subsequent round of least-squares adjustment of the correct stereochemical model gave R 11·8%.

A difference electron-density distribution showed significant peaks in the regions appropriate to the hydrogen atoms, and these atoms were therefore allowed for in the structure-factor calculations though their co-ordinates were held constant in the least-squares refinement. Convergence was reached at R 10·2%. Further improvement could undoubtedly have been obtained by adopting anisotropic thermal parameters for the sulphur, carbon, and oxygen atoms, but this would have required a considerable amount of computing time and since it would have had little effect on the conformational results we did not consider the extra expenditure justified. Unit weights were used throughout the least-squares calculations.

(*b*) *Compound* (4)

Crystal Data.—$C_{26}H_{31}BrO_5S$, $M = 535·5$, Monoclinic, $a = 9·82$, $b = 11·45$, $c = 11·33$ Å (all $\pm 0·01$ Å), $\beta = 111° 40' \pm 20'$, $U = 1184$ Å^3, $D_m = 1·49$, $Z = 2$, $D_c = 1·50$, $F(000) = 556$. Space group $P2_1$ (C_2^2). Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) = 36·9 cm^{-1}.

Crystallographic Measurements.—Rotation, oscillation, and Weissenberg photographs were taken with Cu-K_α radiation, and precession photographs with Mo-K_α radiation. The lattice parameters were derived from the precession photographs. Multiple-film equi-inclination Weissenberg photographs of the layers $h0$—$10l$ were indexed as prescribed by Bijvoet and Peerdeman.[15] The very weak X-ray intensities were estimated visually, but the great majority of the intensities were measured on a Joyce–Deeley flying-spot integrating microdensitometer. In all, 2222 independent structure amplitudes were derived.

Structure Analysis.—The co-ordinates of the bromine and sulphur atoms were initially obtained from a three-dimensional Patterson synthesis, and subsequent electron-density distributions yielded positions for the carbon and oxygen atoms. Least-squares adjustment of the positional and isotropic thermal parameters led to R 14·0%, and when the bromine atom was assigned an anisotropic temperature factor further refinement gave R 11·5%.

The absolute configuration of the derivative was tested by Bijvoet's anomalous-dispersion method. For the absolute configuration shown in (4) R was 11·47%, whereas for the alternative absolute configuration R was 11·53%. As the difference between these two values is small, further least-squares refinement incorporating dispersion corrections was carried out for both models, to give R 11·19% for (4) and 11·26% for the mirror image of (4). The difference between these results, though small, is consistent with the accepted absolute configuration of kaurane derivatives.[2]

A difference electron-density distribution was calculated, and showed peaks in stereochemically acceptable positions for the hydrogen atoms. These were then included in the structure-factor calculations, and further least-squares adjustment of the carbon, oxygen, and sulphur parameters converged at R 10·8%. Unit weights were used throughout the least-squares calculations.

The calculations were performed on the ICL 1905 computer of the University of Sussex and the Atlas computer at the S.R.C. Chilton Laboratory. We thank the S.R.C. for financial support.

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[15] J. M. Bijvoet and A. F. Peerdeman, *Acta Cryst.*, 1956, **9**, 1012.