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Structure and Absolute Configuration of (12*S*,13*S*)-8,12;12,15-Diepoxy-13-bromolabdane

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Abstract. $C_{20}H_{33}BrO_2$, $M_r = 385.37$, monoclinic, $P2_1$, $a = 8.8023$ (5), $b = 9.4861$ (4), $c = 11.857$ (1) Å, $\beta = 95.81$ (1)°, $U = 985.0$ (2) Å^3, $Z = 2$, $D_x = 1.299$ g cm^{-3}, μ(Mo $K\alpha$) = 21.5 cm^{-1}, m.p. 112–113°C. The structure was refined to an R factor of 0.050 including 2134 Friedel pairs. Refinement and Bijvoet indices establish S configurations for atoms C(12) and C(13).

Introduction. All measurements for a crystal 0.32 × 0.45 × 0.29 mm, kindly supplied by Professor A. G. Gonzalez (University of La Laguna, Spain), were made on a PW 1100 computer-controlled four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit of the setting angles for 36 reflexions. Intensities of 3044 independent Friedel pairs were measured up to $\theta = 30°$ using the $\omega/2\theta$ scan technique. No crystal decomposition was observed during the data-collection process. After correction for absorption, Lorentz and polarization effects, 2134 Friedel pairs were considered as observed according to the criterion $I > 2\sigma(I)$ and were used in the calculations. The structure was solved by the heavy-atom method and refined by anisotropic (fixed isotropic for H atoms) full-matrix least-squares analysis. A convenient weighting scheme to prevent bias in $w(F_o - F_c)^2$ was $w = 1/\sigma^2$ with $\sigma = a + b|F_o|$ (coefficients given in Table 1), calculated by the program *PESOS* (Martínez-Ripoll & Cano, 1975). Table 2 shows a list of the final atomic parameters.*

Table 1. *Coefficients for the weighting scheme*

	a	b
$0 < F_o \leq 3.7$	1.27	−0.20
$3.7 < F_o \leq 5.7$	0.71	−0.01
$5.7 < F_o$	0.34	0.05

Table 2. *Atomic positional parameters* (×10^4, *for* Br ×10^5, *for* H ×10^3) *and* H-*atom isotropic thermal parameters* (×10^3)

	x	y	z
Br	−9301 (4)	93018 (0)	71268 (4)
C(1)	3164 (5)	5019 (4)	6012 (3)
C(2)	3975 (6)	3876 (5)	5386 (4)
C(3)	5653 (5)	4226 (6)	5326 (3)
C(4)	6565 (4)	4486 (5)	6485 (3)
C(5)	5680 (4)	5625 (4)	7118 (3)
C(6)	6482 (4)	6124 (4)	8260 (3)
C(7)	5760 (4)	7460 (4)	8715 (3)
C(8)	4089 (4)	7173 (4)	8825 (3)
C(9)	3340 (3)	6662 (3)	7668 (3)
C(10)	3958 (3)	5288 (3)	7215 (3)
C(11)	1652 (4)	6892 (4)	7778 (4)
C(12)	1665 (4)	8221 (4)	8516 (3)
C(13)	1093 (4)	9637 (4)	7992 (3)
C(14)	794 (6)	10441 (5)	9069 (5)
C(15)	240 (5)	9346 (8)	9820 (4)
C(16)	2106 (7)	10320 (5)	7197 (4)
C(17)	3906 (5)	6274 (5)	9879 (3)
C(18)	6867 (6)	3097 (5)	7133 (4)
C(19)	8136 (5)	5083 (6)	6269 (5)
C(20)	3650 (5)	4019 (3)	7957 (4)
O(1)	3232 (3)	8465 (3)	8943 (2)
O(2)	761 (4)	8002 (4)	9428 (3)

	x	y	z	U(Å^2)
H(11)	219 (6)	480 (6)	604 (4)	41
H(12)	327 (6)	587 (7)	551 (5)	41
H(21)	336 (7)	371 (7)	466 (5)	48
H(22)	391 (7)	292 (8)	583 (5)	48
H(31)	570 (7)	505 (9)	494 (6)	55
H(32)	619 (7)	356 (8)	495 (6)	55
H(51)	575 (5)	640 (6)	668 (4)	31
H(61)	745 (6)	628 (7)	810 (5)	41
H(62)	655 (6)	543 (7)	885 (5)	41
H(71)	622 (6)	763 (7)	954 (5)	40
H(72)	580 (6)	818 (7)	821 (4)	40
H(91)	364 (6)	741 (6)	718 (4)	30
H(111)	120 (6)	707 (7)	709 (4)	36
H(112)	122 (6)	621 (7)	810 (4)	36
H(141)	184 (7)	1071 (8)	941 (5)	51
H(142)	19 (7)	118 (8)	892 (5)	51
H(151)	70 (8)	952 (12)	1067 (6)	73
H(152)	−96 (7)	916 (13)	972 (6)	73
H(161)	207 (6)	974 (7)	646 (5)	50

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33248 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (*cont.*)

	x	*y*	*z*	U(Å^2)
H(162)	298 (7)	1048 (7)	768 (5)	50
H(163)	146 (9)	1096 (10)	677 (6)	73
H(171)	294 (7)	601 (8)	995 (5)	54
H(172)	416 (7)	692 (8)	1052 (5)	54
H(173)	463 (7)	568 (8)	999 (6)	54
H(181)	737 (7)	334 (8)	801 (5)	55
H(182)	758 (7)	244 (8)	683 (5)	55
H(183)	606 (7)	260 (8)	718 (5)	55
H(191)	872 (7)	505 (9)	683 (6)	64
H(192)	792 (8)	584 (9)	595 (6)	64
H(193)	859 (7)	457 (10)	573 (5)	64
H(201)	278 (7)	417 (7)	813 (5)	54
H(202)	438 (7)	407 (7)	854 (5)	54
H(203)	365 (7)	305 (8)	759 (5)	54

The absolute configuration was confirmed after refinement of both enantiomers with conventional residuals $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}050$ and 0·077 {weighted residuals being $R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2} = 0{\cdot}071$ and 0·112 respectively}. Moreover, this was tested by comparing the 37 more relevant Bijvoet pairs giving the following discrepancy indices calculated by the program *CONFAB* (Martinez-Ripoll & Fayos, 1977): average Bijvoet difference $R_1 = \Sigma|[F_o(+h) - F_o(-h)] - [F_c(+h) - F_c(-h)]|/N =$

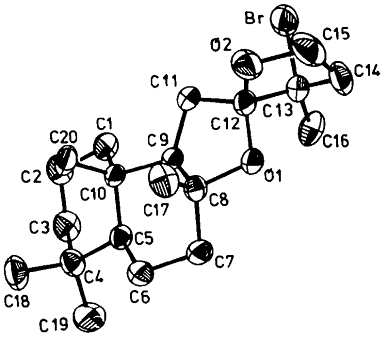

Fig. 1. *ORTEP* drawing (Johnson, 1965) of $C_{20}H_{33}BrO_2$. For the sake of clarity no H atoms are represented. Thermal ellipsoids are scaled to 50% probability.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *for* $C_{20}H_{33}BrO_2$

Average least-squares standard deviations are 0·005 Å and 0·3 °.

C(1)–C(2)	1·530	C(9)–C(10)	1·530
–C(10)	1·545	–C(11)	1·521
C(2)–C(3)	1·522	C(10)–C(20)	1·531
C(3)–C(4)	1·539	C(11)–C(12)	1·534
C(4)–C(5)	1·567	C(12)–C(13)	1·543
–C(18)	1·536	–O(1)	1·439
–C(19)	1·540	–O(2)	1·421
C(5)–C(6)	1·537	C(13)–C(14)	1·533
–C(10)	1·565	–C(16)	1·508
C(6)–C(7)	1·539	–Br	1·989
C(7)–C(8)	1·514	C(14)–C(15)	1·482
C(8)–C(9)	1·540	C(15)–O(2)	1·447
–C(17)	1·535		
–O(1)	1·454		
C(2)–C(1)–C(10)	112·1	C(1)–C(10)–C(9)	108·7
C(1)–C(2)–C(3)	111·8	C(1)–C(10)–C(20)	108·1
C(2)–C(3)–C(4)	114·5	C(5)–C(10)–C(9)	103·5
C(3)–C(4)–C(5)	107·4	C(5)–C(10)–C(20)	115·6
C(3)–C(4)–C(18)	110·9	C(9)–C(10)–C(20)	112·3
C(3)–C(4)–C(19)	107·9	C(9)–C(11)–C(12)	102·5
C(5)–C(4)–C(18)	114·9	C(11)–C(12)–C(13)	120·1
C(5)–C(4)–C(19)	108·9	C(11)–C(12)–O(1)	106·6
C(18)–C(4)–C(19)	106·6	C(11)–C(12)–O(2)	109·9
C(4)–C(5)–C(6)	115·4	C(13)–C(12)–O(1)	105·3
C(4)–C(5)–C(10)	115·2	C(13)–C(12)–O(2)	104·4
C(5)–C(6)–C(7)	113·2	O(1)–C(12)–O(2)	110·3
C(6)–C(7)–C(8)	108·7	C(12)–C(13)–C(14)	100·0
C(7)–C(8)–C(9)	108·2	C(12)–C(13)–C(16)	115·9
C(7)–C(8)–C(17)	110·7	C(12)–C(13)–Br	107·9
C(7)–C(8)–O(1)	112·0	C(14)–C(13)–C(16)	118·0
C(9)–C(8)–C(17)	118·7	C(14)–C(13)–Br	106·8
C(9)–C(8)–O(1)	99·9	C(16)–C(13)–Br	107·6
C(17)–C(8)–O(1)	107·0	C(13) C(14) C(15)	104·3
C(8)–C(9)–C(10)	116·4	C(14)–C(15)–O(2)	106·9
C(8)–C(9)–C(11)	102·3	C(8)–O(1)–C(12)	108·6
C(10)–C(9)–C(11)	122·6	C(12)–O(2)–C(15)	109·6
C(1)–C(10)–C(5)	108·5		

Table 4. *Torsion angles* (°) *for* $C_{20}H_{33}BrO_2$

Average standard deviations are 0·5 °.

C(1)–C(2)–C(3)–C(4)	56·0	O(1)–C(12)–C(11)–C(9)	−11·2	C(17)–C(8)–C(9)–C(10)	−65·1
C(2)–C(3)–C(4)–C(5)	−52·6	C(12)–C(11)–C(9)–C(8)	34·0	C(17)–C(8)–O(1)–C(12)	−85·4
C(3)–C(4)–C(5)–C(10)	53·3	C(13)–C(12)–O(2)–C(15)	−25·7	C(17)–C(8)–C(7)–C(6)	76·6
C(4)–C(5)–C(10)–C(1)	−55·0	C(12)–O(2)–C(15)–C(14)	2·9	C(20)–C(10)–C(5)–C(6)	−67·2
C(5)–C(10)–C(1)–C(2)	54·3	O(2)–C(15)–C(14)–C(13)	21·3	C(20)–C(10)–C(5)–C(4)	66·5
C(10)–C(1)–C(2)–C(3)	−55·9	C(15)–C(14)–C(13)–C(12)	−35·1	C(20)–C(10)–C(9)–C(8)	65·2
C(9)–C(10)–C(5)–C(6)	56·0	C(14)–C(13)–C(12)–O(2)	37·1	C(20)–C(10)–C(9)–C(11)	−61·6
C(10)–C(5)–C(6)–C(7)	−59·4	C(10)–C(9)–C(8)–O(1)	179·3	C(20)–C(10)–C(1)–C(2)	−71·7
C(5)–C(6)–C(7)–C(8)	57·4	C(8)–C(9)–C(10)–C(1)	−175·3	C(18)–C(4)–C(3)–C(2)	73·7
C(6)–C(7)–C(8)–C(9)	−55·0	C(11)–C(9)–C(8)–C(7)	−161·7	C(18)–C(4)–C(5)–C(10)	−70·7
C(7)–C(8)–C(9)–C(10)	62·1	C(16)–C(13)–C(12)–C(11)	−71·1	C(18)–C(4)–C(5)–C(6)	61·0
C(8)–C(9)–C(10)–C(5)	−60·1	C(16)–C(13)–C(12)–O(1)	48·9	C(19)–C(4)–C(3)–C(2)	−169·9
C(11)–C(9)–C(8)–O(1)	−44·4	C(16)–C(13)–C(12)–O(2)	165·1	C(19)–C(4)–C(5)–C(10)	169·9
C(9)–C(8)–O(1)–C(12)	38·8	C(16)–C(13)–C(14)–C(15)	−161·6	C(19)–C(4)–C(5)–C(6)	−58·5
C(8)–O(1)–C(12)–C(11)	−17·9	C(17)–C(8)–C(9)–C(11)	71·2		

Table 5. *Deviations* (Å) *of some atoms from the best ring planes of the molecule*

Atoms not used in the plane calculations are indicated by an asterisk.

Plane 1		Plane 2	
C(1)	0·234	C(5)	−0·248
C(2)	−0·231	C(6)	0·246
C(3)	0·221	C(7)	−0·229
C(4)	−0·219	C(8)	0·242
C(5)	0·232	C(9)	−0·263
C(10)	−0·237	C(10)	0·251

Plane 3		Plane 4	
*C(8)	0·645	C(12)	0·010
C(9)	−0·041	*C(13)	−0·593
C(11)	0·063	C(14)	−0·009
C(12)	−0·066	C(15)	0·015
O(1)	0·045	O(2)	−0·016

The equations of the planes expressed in direct space as $AX + BY + CZ = D$

Plane	A	B	C	D
1	0·7973	8·0574	−6·2419	0·3096
2	−1·0902	−6·9012	8·1089	1·5188
3	−0·8441	−6·0394	9·1408	2·7451
4	6·7261	0·9090	6·6085	7·4857

Angles between planes

Plane 1/plane 2	11·5°	Plane 2/plane 3	7·5°
Plane 1/plane 3	18·7	Plane 3/plane 4	69·3

0·43 (7·70 for the enantiomorph) and average Bijvoet ratio $R_2 = \Sigma\,|R_o - R_c|/N = 0{\cdot}04\ (0{\cdot}82)$, with $R_o = [F_o(+h)^2 - F_o(-h)^2]/\langle F_o^2\rangle$, $R_c = [F_c(+h)^2 - F_c(-h)^2]/\langle F_c^2\rangle$, and N = number of Bijvoet pairs.

Discussion. Recent interest in several labdanolic diterpenes (Gonzalez, Francisco, Freire, Hernandez, Salazar & Suarez, 1976*a*,*b*) justifies the present X-ray analysis.

The absolute configuration of the molecule, shown in Fig. 1, establishes *S* configurations for atoms C(12) and C(13). A list of bond lengths and bond angles is shown in Table 3. Torsion angles are listed in Table 4.

The least-squares ring planes in the molecule have been calculated (Schomaker, Waser, Marsh & Bergman, 1959) and are shown in Table 5. The two six-membered rings of the labdane skeleton have chair conformations. The two five-membered rings both have an approximate envelope conformation, C(8) and C(13) being at the flaps.

Electronic repulsion between the three methyl groups at C(17), C(18) and C(20) causes a bending effect on the main plain of the molecule. Distances between these groups are C(17)–C(20) = 3·117 and C(18)–C(20) = 3·208 Å. All intermolecular distances are of the order of van der Waals contacts.

Most of the calculations were performed with the XRAY 70 system of crystallographic programs (Stewart, Kundell & Baldwin, 1970). We wish to thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Spain, for the facilities provided on the Univac 1108 computer.

References

GONZALEZ, A. G., FRANCISCO, C. G., FREIRE, R., HERNANDEZ, R., SALAZAR, J. A. & SUAREZ, E. (1976*a*). *Tetrahedron Lett.* **22**, 1897–1898.

GONZALEZ, A. G., FRANCISCO, C. G., FREIRE, R., HERNANDEZ, R., SALAZAR, J. A. & SUAREZ, E. (1976*b*). *Tetrahedron Lett.* **31**, 2725–2728.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS* program. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid 6, Spain.

MARTÍNEZ-RIPOLL, M. & FAYOS, J. (1977). *CONFAB* program. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid 6, Spain.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.