Tableau 5. *Distances de contact van der Waals* (*distances intermoléculaires*)

	Distances (Å)		Symétrie	
O(1)—H(10)	2,89	$1+x$	y	z
O(1)—H(8)	3,15	$-1+x$	y	z
O(2)—H(11)	2,51	$-x$	$1-y$	$1-z$
O(2)—H(8)	2,94	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
C(2)—H(1)	2,63	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
C(13)–H(3)	3,00	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
C(3)—O(2)	3,51	$-1+x$	y	z
C(3)—O(2)	3,55	$-x$	$1-y$	$1-z$
C(3)—C(4)	3,65	$1-x$	$1-y$	$1-z$
C(3)—C(9)	3,41	$1-x$	$1-y$	$1-z$
C(7)—O(1)	3,34	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
C(8)—O(1)	3,36	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

ment (SOCH$_3$) provoque un effet de recouvrement anti-liant sur la liaison π de la double liaison vinylique, il en résulte de ce fait un rallongement de la distance C(1)–C(2) [égale à 1,390 (9) Å et noté C(15)–C(16) dans le papier précédent (Tranqui & Fillion, 1972)].

Le groupe sulfone est relié à la molécule par l'intermédiaire du carbone C(1); la liaison S–C(1) est de 1,734 (4) Å, par ailleurs l'atome du soufre est d'une part lié aux deux oxygènes O(1) et O(2), les distances S–O(1) et S–O(2) sont respectivement 1,452 (4) et 1,448 (3) Å et d'autre part, au carbone méthylique C(3) avec S–C(3) égale à 1,762 (6) Å. Les valeurs des angles O–S–O, C–S–O et C–S–C (Tableau 3) montrent que le tétraèdre formé par S, O(1), O(2) et CH$_3$ est très déformé, l'angle O(1)–S–O(2) très ouvert (117°) indique qu'il y a une répulsion notable entre les oxygènes du groupe sulfone.

(b) *Cohésion cristalline*

Nous avons consigné dans le Tableau 5 les liaisons intermoléculaires assurant la cohésion cristalline, certaines de ces liaisons sont particulièrement courtes [O(2)–H(11) = 2,51, C(1)–O(2) = 3,20, C(3)–C(9) = 3,41, C(13)–H(3) = 3,00 Å] en admettant que les rayons de van der Waals des atomes O, C, H sont respectivement 1,4; 2,0; 1,2 Å (Pauling, 1965). Par ailleurs, l'existence des distances intermoléculaires de type C–H montre, comme nous l'avons déjà signalé dans les précédentes notes, que la cohésion moléculaire dans ces types de composés est assurée surtout par les contacts carbone–hydrogène.

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The Conformations of Tetracyclic Diterpenes. IV.* The Crystal and Molecular Structure of a Minor Product of Oxidative Cleavage of Methyl *ent*-Trachyloban-19-oate with Thallic Acetate

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Crystals of the oxidative cleavage product are orthorhombic, $a = 8.430 (1)$, $b = 9.871 (2)$, $c = 23.060 (4)$ Å, $Z = 4$, space group $P2_12_12_1$. The structure was solved by direct methods and refined by least-squares procedures to $R = 0.040$ for 1202 observed reflexions. The conformations of rings A and B as well as the bicyclo[2,2,2]octyl system may be attributed, at least in part, to intramolecular steric interactions. The molecules are linked in chains parallel to [010] by hydrogen bonds between the hydroxyl groups of neighbouring molecules.

Introduction

Structures have been assigned to all but one of the products isolated from the complex mixture obtained

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* Part III: *Acta Cryst.* (1976). B32, 24–30.

by reaction of methyl *ent*-trachyloban-19-oate (I) with thallic acetate (Campbell, Gunn, McAlees & McCrindle, 1973, 1975). A tentative structure (IIa) was advanced for this product on the basis of spectroscopic evidence and mechanistic considerations (Campbell *et al.*, 1975); however, this structure was incon-

sistent with the resistance of the corresponding diol (II*b*) to cleavage by periodate (McAlees, McCrindle & Murphy, 1975). Only very small quantities of the compound were available, but fortunately crystals of the diol proved suitable for X-ray analysis, and the structure determination was undertaken to elucidate the structure and to examine the conformation of the molecule in general and the bicyclic ring system in particular.
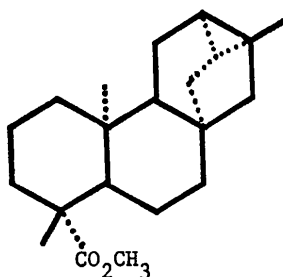
(I)
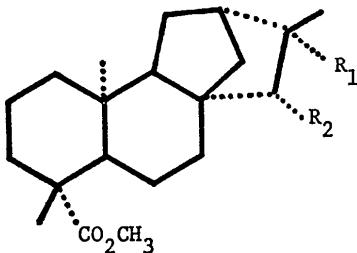
(IIa) $R_1=R_2=OCOCH_3$

(IIb) $R_1=R_2=OH$
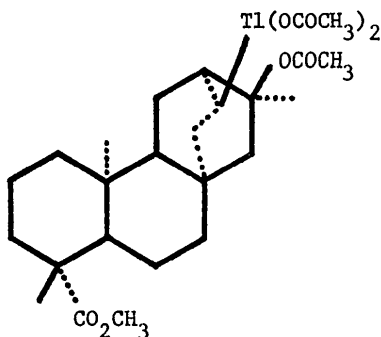
(III)

Experimental

Crystals of the diol (II*b*) crystallized as regular prisms elongated along [100]. Unit-cell parameters were obtained by least-squares procedures from the Bragg angles of 12 reflexions with non-zero Miller indices measured on a Hilger and Watts diffractometer.

Crystal data

$C_{21}H_{34}O_4$, $M = 350·5$. Orthorhombic, $a = 8·430$ (1), $b = 9·871$ (2), $c = 23·060$ (4) Å, $U = 1918·9$ Å^3, $D_c = 1·21$ g cm^{-3}, $Z = 4$, $F(000) = 768$. λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·5 cm^{-1}. The systematic absences $h00$, h odd; $0k0$, k odd; $00l$, l odd uniquely determine the space group to be $P2_12_12_1(D_2^4)$.

Intensities were collected out to $\theta = 23°$ (θ–2θ scan, 70 measurement steps of 1 s at 0·01° intervals, 17·5 s stationary background counts at beginning and end of each scan) on a PDP-8I controlled Hilger and Watts Y 290 four-circle diffractometer equipped with a scintillation counter and graphite monochromator. Lorentz and polarization factors were applied and the structure amplitudes derived; of the 1563 unique data, 1202 reflexions had intensities greater than 3σ above background $\{\sigma^2(I) = [S + 4(B_1 + B_2) + (0·05\ S)^2]$ with S the scan count and B_1 and B_2 the background counts} while the remaining 361 less than 3σ above background were taken as unobserved.

Structure analysis

The data were placed on an absolute scale (Wilson, 1942) and the normalized structure amplitudes derived. The initial attempt to solve the phase problem was based on the 250 reflexions with $E > 1·35$, using MULTAN (Germain, Main & Woolfson, 1971). The solution that produced the highest figure of merit and the lowest residual $[(\sum|E_o - E_c|)/\sum E_o]$ yielded an E map in which 24 atoms of a diterpenoid structure containing not the expected bicyclo[3,2,1]octane but a bicyclo[2,2,2]octane ring system could be recognized. The remaining atom was located from an $|F_o - F_c|$ synthesis. Initial full-matrix least-squares refinement with all atoms assigned isotropic temperature factors gave R 0·113. At this stage the two hydroxyl O atoms were identified on the basis of bond lengths and temperature factors. All H atoms (except for the two hydroxyl H's) were then added to the structure factor calculation in calculated positions but were not refined; R decreased to 0·083. The hydroxyl H atoms were located unambiguously from a second $|F_o - F_c|$ synthesis and the refinement was completed with all C and O atoms assigned anisotropic temperature factors. The final R was 0·040 for the 1202 observed and 0·054 for all 1563 data. The scattering curves for O and C are from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The weights in the final states of refinement were $w = 0$ for the unobserved and $w = 1/[\sigma(F_o)^2 + 0·0034F_o^2]$ for the observed reflexions; the validity of the scheme judged by the variation of

Table 1. *Coordinates and thermal parameters*

(*a*) Fractional coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z		x	y	z
O(1)	−985 (5)	5848 (3)	245 (1)	C(10)	1637 (5)	4453 (4)	1461 (2)
O(2)	−165 (5)	7653 (3)	724 (1)	C(11)	4029 (5)	2917 (4)	1758 (2)
O(3)	4254 (4)	2765 (3)	2377 (1)	C(12)	4794 (5)	1717 (4)	1439 (2)
O(4)	4303 (4)	101 (3)	2222 (1)	C(13)	4023 (5)	366 (4)	1612 (2)
C(1)	1916 (5)	5363 (4)	1998 (2)	C(14)	2198 (6)	497 (4)	1502 (2)
C(2)	1141 (6)	6754 (4)	1938 (2)	C(15)	2784 (5)	1862 (4)	633 (2)
C(3)	−615 (6)	6652 (4)	1808 (2)	C(16)	4558 (6)	1961 (5)	785 (2)
C(4)	−1038 (5)	5749 (4)	1287 (2)	C(17)	−2868 (6)	5545 (5)	1295 (2)
C(5)	−187 (5)	4346 (4)	1360 (2)	C(18)	−721 (5)	6390 (4)	699 (2)
C(6)	−597 (5)	3286 (4)	895 (2)	C(19)	138 (9)	8302 (6)	174 (2)
C(7)	1 (5)	1893 (4)	1076 (2)	C(20)	4737 (7)	−837 (5)	1299 (2)
C(8)	1784 (5)	1832 (4)	1198 (2)	C(21)	2488 (5)	5086 (4)	933 (2)
C(9)	2237 (5)	2992 (4)	1617 (2)				

(*b*) Anisotropic thermal parameters U_{ij} ($\text{Å}^2 \times 10^2$) in the expression $\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right]$ with estimated standard deviations in parentheses

|	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	10·3 (3)	4·3 (2)	3·6 (2)	−1·2 (2)	−1·6 (2)	0·3 (1)
O(2)	8·8 (3)	3·9 (2)	4·0 (2)	−1·2 (2)	−0·6 (2)	0·3 (1)
O(3)	6·9 (2)	3·5 (2)	3·5 (1)	−0·4 (2)	−2·4 (1)	0·3 (1)
O(4)	6·8 (2)	3·9 (2)	3·4 (2)	0·7 (2)	−1·8 (1)	0·3 (1)
C(1)	5·4 (3)	3·0 (2)	3·2 (2)	−0·1 (2)	−0·8 (2)	−0·4 (2)
C(2)	6·8 (3)	3·4 (2)	3·7 (2)	0·2 (2)	−1·2 (2)	−1·2 (2)
C(3)	6·0 (3)	3·4 (2)	3·5 (2)	0·7 (2)	0·2 (2)	−0·5 (2)
C(4)	3·2 (2)	3·6 (2)	3·9 (2)	0·5 (2)	0·4 (2)	0·1 (2)
C(5)	3·2 (2)	2·8 (2)	2·9 (2)	−0·3 (2)	0·1 (2)	0·1 (2)
C(6)	3·8 (2)	3·2 (2)	4·1 (2)	−0·2 (2)	−0·9 (2)	−0·1 (2)
C(7)	4·1 (3)	3·2 (2)	5·1 (2)	−0·7 (2)	−1·6 (2)	−0·2 (2)
C(8)	4·0 (2)	2·7 (2)	2·9 (2)	−0·6 (2)	−0·6 (2)	0·1 (2)
C(9)	3·4 (2)	3·1 (2)	2·4 (2)	−0·1 (2)	−0·1 (2)	0·5 (2)
C(10)	3·6 (2)	2·5 (2)	2·8 (2)	−0·3 (2)	−0·5 (2)	0·1 (2)
C(11)	3·9 (2)	3·5 (2)	3·3 (2)	−0·2 (2)	−1·0 (2)	0·2 (2)
C(12)	3·3 (2)	3·8 (2)	4·0 (2)	0·4 (2)	−0·6 (2)	0·4 (2)
C(13)	4·8 (3)	3·7 (2)	3·2 (2)	0·7 (2)	−1·0 (2)	0·1 (2)
C(14)	5·3 (3)	3·1 (2)	3·5 (2)	0·0 (2)	−0·7 (2)	0·0 (2)
C(15)	4·7 (3)	3·9 (2)	2·7 (2)	0·5 (2)	−0·3 (2)	−0·2 (2)
C(16)	4·7 (3)	4·6 (3)	4·1 (2)	0·7 (2)	0·5 (2)	0·8 (2)
C(17)	3·8 (3)	4·8 (3)	7·2 (3)	0·6 (2)	0·8 (2)	0·5 (3)
C(18)	4·1 (3)	2·8 (2)	4·0 (2)	−0·1 (2)	−0·8 (2)	−0·2 (2)
C(19)	12·2 (5)	5·7 (3)	4·7 (3)	−2·2 (4)	−0·2 (3)	1·8 (3)
C(20)	7·0 (4)	4·6 (3)	5·3 (3)	1·7 (3)	−0·8 (3)	−0·3 (3)
C(21)	3·4 (2)	3·9 (2)	3·8 (2)	−0·3 (2)	0·1 (2)	0·9 (2)
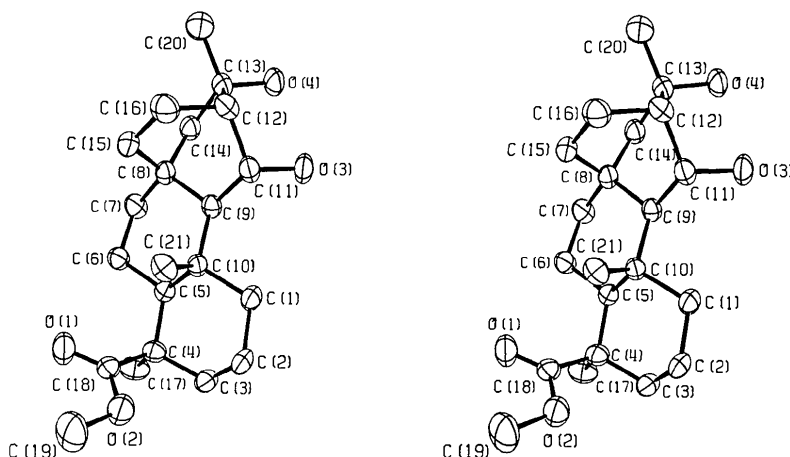
Fig. 1. Stereo diagram of (II*b*); the thermal ellipsoids shown are at the 50% probability level.

$w\Delta^2$ over ranges of $\sin \theta/\lambda$ and $|F_o|$ was satisfactory. The final weighted R ($[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$) was 0·057.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31355 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses*

C(1)–C(2)	1·527 (6)	C(9)—C(10)	1·569 (6)
C(1)–C(10)	1·548 (6)	C(9)—C(11)	1·547 (6)
C(2)–C(3)	1·513 (7)	C(10)–C(21)	1·545 (6)
C(3)–C(4)	1·538 (6)	C(11)–C(12)	1·536 (6)
C(4)–C(5)	1·569 (6)	C(12)–C(13)	1·536 (6)
C(4)–C(17)	1·556 (7)	C(12)–C(16)	1·541 (6)
C(4)–C(18)	1·519 (6)	C(13)–C(14)	1·565 (7)
C(5)–C(6)	1·538 (6)	C(13)–C(20)	1·514 (7)
C(5)–C(10)	1·559 (6)	C(15)–C(16)	1·538 (6)
C(6)–C(7)	1·523 (6)	O(1)—C(18)	1·197 (5)
C(7)–C(8)	1·530 (6)	O(2)—C(18)	1·334 (5)
C(8)–C(9)	1·547 (5)	O(2)—C(19)	1·444 (6)
C(8)–C(14)	1·533 (6)	O(3)—C(11)	1·449 (5)
C(8)–C(15)	1·551 (6)	O(4)—C(13)	1·450 (5)

C(18)O(2)C(19)	116·0 (4)	C(1)C(10)C(5)	108·0 (3)
C(2)C(1)C(10)	112·6 (3)	C(1)C(10)C(9)	107·5 (3)
C(1)C(2)C(3)	112·1 (4)	C(1)C(10)C(21)	109·0 (3)
C(2)C(3)C(4)	114·8 (4)	C(5)C(10)C(9)	106·8 (3)
C(3)C(4)C(5)	108·7 (3)	C(5)C(10)C(21)	111·6 (3)
C(3)C(4)C(17)	107·2 (4)	C(9)C(10)C(21)	113·7 (3)
C(3)C(4)C(18)	114·5 (3)	O(3)C(11)C(9)	109·9 (3)
C(5)C(4)C(17)	109·7 (3)	O(3)C(11)C(12)	109·7 (3)
C(5)C(4)C(18)	112·5 (3)	C(9)C(11)C(12)	110·3 (3)
C(17)C(4)C(18)	103·8 (4)	C(11)C(12)C(13)	111·6 (3)
C(4)C(5)C(6)	115·0 (3)	C(11)C(12)C(16)	107·1 (3)
C(4)C(5)C(10)	114·0 (3)	C(13)C(12)C(16)	109·6 (3)
C(6)C(5)C(10)	111·9 (3)	O(4)C(13)C(12)	109·8 (3)
C(5)C(6)C(7)	110·3 (3)	O(4)C(13)C(14)	109·4 (3)
C(6)C(7)C(8)	114·3 (4)	O(4)C(13)C(20)	104·8 (3)
C(7)C(8)C(9)	109·1 (3)	C(12)C(13)C(14)	107·6 (3)
C(7)C(8)C(14)	110·0 (3)	C(12)C(13)C(20)	112·9 (4)
C(7)C(8)C(15)	112·3 (3)	C(14)C(13)C(20)	112·2 (4)
C(9)C(8)C(14)	107·1 (3)	C(8)C(14)C(13)	111·6 (4)
C(9)C(8)C(15)	112·1 (3)	C(8)C(15)C(16)	109·8 (3)
C(14)C(8)C(15)	106·1 (3)	C(12)C(16)C(15)	109·8 (3)
C(8)C(9)C(10)	117·2 (3)	C(4)C(18)O(1)	124·2 (4)
C(8)C(9)C(11)	109·7 (3)	C(4)C(18)O(2)	114·4 (3)
C(10)C(9)C(11)	114·0 (3)	O(1)C(18)O(2)	121·4 (4)

Final positional and anisotropic thermal parameters are listed in Table 1, bond lengths and angles in Table 2. A stereo view of the molecule produced by ORTEP (Johnson, 1965) illustrating the ellipsoids of thermal motion is shown in Fig. 1. The thermal motion was analysed in terms of the rigid-body modes of translation, libration, and screw motion (Schomaker & Trueblood, 1968). The results indicated that, although there were some small amounts of independent motion of the methyl substituents and acetoxy group, the molecule as a whole approximated a rigid body fairly well; the r.m.s. standard deviation in the U_{ij} (Table 1) was 0·0061 Å² while the r.m.s. ΔU_{ij} was 0·0056 Å². The results of the analysis further suggest that the translational tensor is roughly isotropic, with the librational tensor somewhat more anisotropic; not unexpectedly the largest principal axis of libration is approximately parallel to the longest dimension of the molecule. The bond distances and angles were corrected for libration (Cruickshank, 1956, 1961); however the values listed in Table 2 were altered by less than 1σ and the corrected values are not given.

Discussion

We have previously reported the structures of several tetracyclic diterpenes containing either a bicyclo[3,2,1]-octane (Ferguson & Marsh, 1975a, b) or a bicyclo-[2,2,2]octane ring system (Ferguson & Marsh, 1976). The structure of each of these molecules could be rationalized with some success in terms of the rather severe degree of intermolecular steric crowding. The
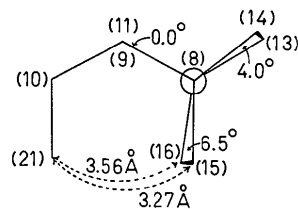
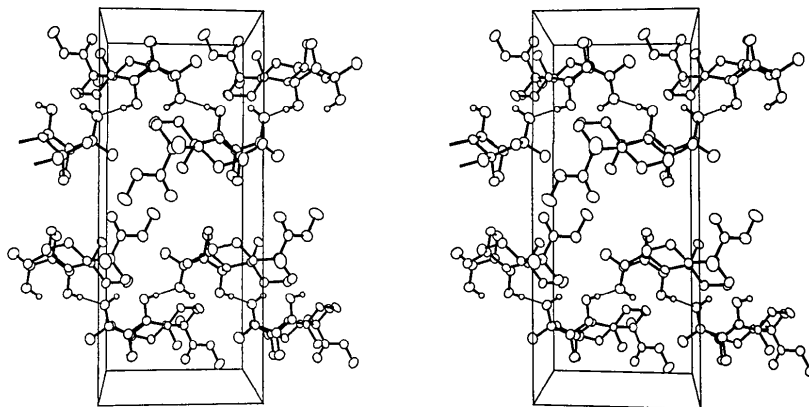Fig. 2. Newman projection along the C(8)···C(12) vector.

Fig. 3. Stereo diagram of the molecular packing. The origin is at the bottom left hand corner with x pointing towards the viewer, $y \rightarrow$, and $z \uparrow$.

Table 3. Intra-annular torsion angles

(a) Ring A

C(10)C(1)–C(2)C(3)	55·1		C(3)C(4)–C(5)C(10)	−53·4
C(1)C(2)—C(3)C(4)	−52·8		C(4)C(5)–C(10)C(1)	56·3
C(2)C(3)—C(4)C(5)	50·7		C(2)C(1)–C(10)C(5)	−55·8

(b) Ring B

C(6)C(5)—C(10)C(9)	−55·7		C(6)C(7)–C(8)C(9)	50·3
C(10)C(5)–C(6)C(7)	60·0		C(7)C(8)–C(9)C(10)	−49·5
C(5)C(6)—C(7)C(8)	−57·1		C(8)C(9)–C(10)C(5)	52·3

(c) The bicyclo[2,2,2]octane moiety

	Present structure	BAO	BOC	BSO
C(8)C(9)——C(11)C(12)*	0·0	−0·9	−0·4	4·7
C(8)C(15)—C(16)C(12)	11·0	3·5	−0·1	5·1
C(8)C(14)—C(13)C(12)	6·6	−5·4	−0·6	5·4
C(11)C(9)—C(8)C(15)	−56·6	−54·9	−59·6	−61·4
C(11)C(9)—C(8)C(14)	59·4	58·9	59·0	54·0
C(16)C(15)–C(8)C(9)	50·4	53·7	59·4	55·1
C(16)C(15)–C(8)C(14)	−66·2	−61·0	−60·1	−59·3
C(13)C(14)–C(8)C(9)	−63·9	−55·3	−58·2	−60·6
C(13)C(14)–C(8)C(15)	56·0	62·0	60·6	53·9
C(9)C(11)—C(12)C(16)	60·5	59·3	60·0	57·3
C(9)C(11)—C(12)C(13)	−59·4	−61·1	−58·3	−62·5
C(15)C(16)–C(12)C(11)	−67·1	−60·2	−59·5	−63·7
C(15)C(16)–C(12)C(13)	54·1	56·5	59·6	56·0
C(14)C(13)——C(12)C(11)	54·8	63·9	59·0	57·1
C(14)C(13)——C(12)C(13)	−63·6	−55·2	−59·5	−61·8
C(9)C(8)·····C(12)C(11)	0·0	−0·5	−0·2	2·8
C(15)C(8)····C(12)C(16)	6·5	2·0	0·0	3·0
C(14)C(8)····C(12)C(13)	4·0	−3·2	−0·3	3·1

* The numbering scheme is that for the present structure.

potential for similar intramolecular steric interactions is also present in this structure.

The conformations of the various parts of the molecule may be described in terms of the intra-annular torsion angles listed in Table 3. Ring A possesses a chair slightly flattened in the region of C(3)–C(4). There are short cross-ring contacts between the C(21) methyl group and C(18), O(1), and O(2) of the acetoxy side chain [3·044 (6), 3·415 (6), and 3·414 (6) Å respectively], and the ring A flattening may be attributed, at least in part, to relief of these trans-annular interactions. Ring A flattening to varying extents has been observed in a large number of structures (Ferguson & Marsh, 1975a, 1976; Ferguson, Macaulay, Midgley, Robertson & Whalley, 1970; Rendle, 1972) containing similar cross-ring steric crowding. Interestingly though, the structure of (III) (Ferguson & Marsh, 1975b) also had similar steric interactions, but ring A had a virtually ideal chair conformation. As we have pointed out earlier (Ferguson & Marsh, 1976), the inclusion of cross-ring interactions alone to explain such occasional ring A deformations, while apparently successful in some instances, appears to be an oversimplification.

Ring B also adopts a chair conformation; the C(8)C(9)C(10) end is considerably flattened with a concomitant increased puckering at the opposite C(5)C(6)C(7) end (Table 3). There are short contacts between the C(21) methyl group and C(15) and C(16)

of the bicyclo[2,2,2]octyl moiety [3·266(6) and 3·560 (6) Å respectively] which, together with the junction to the bicyclooctane, most probably determine the observed conformation. In another diterpene containing a bicyclo[2,2,2]octane system, methyl *ent*-16-β-*p*-bromobenzyloxy-17(16 → 12)*abeo*-atisan-19-oate (Ferguson & Marsh, 1975c), hereinafter referred to as BAO, a similar ring B conformation was found.

In common with the other tetracyclic diterpenes we have examined, the most interesting single feature is the bicyclic ring system, in the present structure a bicyclo[2,2,2]octane. An idealized D_{3h} conformation for bicyclo[2,2,2]octane was found in the 1,4-dicarboxylic acid derivative (Ermer & Dunitz, 1969) (hereinafter BOC) while in 1-*p*-bromobenzenesulphonyloxymethyl-bicyclo[2,2,2]octane (Cameron, Ferguson & Morris, 1968) (hereinafter BSO) a slight rotation about the 1,4-axis resulted in a slightly staggered conformation with nearly D_3 symmetry. Potential energy calculations on the unsubstituted bicyclo[2,2,2]octane (Ermer & Dunitz, 1969) suggested that the conformation of minimum energy may be slightly displaced from the eclipsed D_{3h} form, but that the barrier is only of the order of 0·1 kcal mol^{-1}. In the present structure the conformation of the bicyclic moiety differs substantially from the simple D_{3h} and D_3 forms and is characterized by the torsion angles listed in Table 3 and the Newman projection along the 1,4-axis shown in Fig. 2. In addition Table 3 contains the corresponding torsion angles for BOC, BSO, and BAO. As well as the strains resulting from the incorporation of the bicyclooctane into a fused ring system, the exact conformation adopted is undoubtedly a complex function of the various intra- and inter-molecular forces. Relief of the short contacts between C(21) and C(15) [3·266 (6) Å] and between C(21) and C(16) [3·560 (6) Å] results in a large increase in the C(8)C(9)C(10) angle to 117·2° and somewhat smaller increases in C(15)C(8)C(9) and C(9)C(10)C(21) to 112·1° and 113·7° respectively; there are concomitant decreases in C(15)C(8)C(14) and C(14)C(8)C(9) to 106·1° and 107·1° respectively. C(11)C(12)C(13) has increased to 111·6° as a consequence of the short O(3)···O(4) separation of 2·654 (4) Å. In addition to normal intermolecular steric interactions resulting from the molecular packing, there is also inter- and possibly intra-molecular hydrogen bonding (see below) which helps to determine the exact conformation.

The bond lengths for the most part do not differ significantly from the normal values for the particular bond type (Sutton, 1965). The slightly large values for C(4)–C(5) and C(9)–C(10) [1·569 (6) Å] may reflect the tendency to relieve the high degree of steric interaction involving the C(21) methyl group. C(2)–C(3), 1·513 (6) Å, is anomalously short and interestingly this same bond has been found to be short in other tetracyclic diterpenoid structures (Ferguson & Marsh, 1975a, b, 1976). There seems, however, to be no apparent explanation.

The molecular packing is illustrated in Fig. 3. The

molecules are linked in chains parallel to [010] by hydrogen bonds between the hydroxyl groups of neighbouring molecules, with each molecule involved in two hydrogen bonds, one as donor and one as acceptor. For clarity the H atoms bonded to O(3) and O(4) are shown; their positions were clearly revealed by an $|F_o - F_c|$ synthesis although they were not included in the refinement. The pertinent interatomic distances and angles are listed in Table 4(a) and agree well with accepted values (Hamilton & Ibers, 1968). There is also a possible intramolecular hydrogen bond (not shown in Fig. 3) between the two hydroxyl groups, but the geometry is somewhat less favourable than for the intermolecular situation. Table 4(b) contains the pertinent interatomic distances and angles.

Table 4. *Hydrogen bonding*

(a) Intermolecular hydrogen-bond parameters

O(3)——H(O3) 0·87 Å	C(11)——O(3)——H(O3) 106°
H(O3)···O(4') 1·91	O(3)——H(O3)···O(4') 168
	H(O3)···O(4')——C(13') 123

Primed atoms belong to the molecule at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

(b) Intramolecular hydrogen-bond parameters

O(4)——H(O4) 0·98 Å	C(13)——O(4)——H(O4) 113°
H(O4)···O(3) 1·83	O(4)——H(O4)···O(3) 140
	H(O4)···O(3)——C(11) 102

The remaining intermolecular contacts correspond to van der Waals interactions, the shortest being between O(3) of the reference molecule (Table 1) and C(20) of the molecule at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ (3·456 Å).

Finally a brief word about the proposed mechanism. Formally, like all other oxidative cleavage products isolated (Campbell, Gunn, McAlees & McCrindle, 1973, 1975), (IIa) derives from electrophilic attack on C(13)–C(16) in methyl *ent*-trachyloban-19-oate. It presumably arises from intermediate (III) by heterolysis of the –Tl(OAc)$_2$ group, migration of the α-hydride from C(11) to C(13), and capture of solvent at C(11).

were locally modified versions of the X-RAY 72 System (1972).

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