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3β,28-Diacetoxy-18β,19β-epoxylupane

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Abstract. $C_{34}H_{54}O_5$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}088\,(1)$, $b = 11{\cdot}467\,(2)$, $c = 33{\cdot}321\,(8)$ Å (at 295 K), $V = 3090{\cdot}4$ Å^3, $Z = 4$, $M_r = 542{\cdot}8$, $D_c = 1{\cdot}17$ Mg m^{-3}, $F(000) = 1192$, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·079 mm^{-1}. $R = 0{\cdot}035$ for 1765 diffractometer-measured reflections. The structure confirms the β-epoxidation of a pentacyclic triterpene at the *E* ring.

Introduction. 3β,28-Diacetoxy-18β,19β-epoxylupane is a peracid epoxidation product of a pentacyclic triterpene belonging to the lupane group (Suokas, 1977). Epoxidation of triterpenes usually occurs by attack from the α-side due to steric hindrance of methyl groups on the β-side. However, in this case spectral data indicated that peracid oxidation produced a different epoxide from that obtained by ozone treatment (Suokas & Hase, 1977*a*). Further experiments showed that this mechanism was not due to the directive effect of the C(28) acetoxy group on the β-side (Suokas & Hase, 1977*b*). Thus, a crystallographic study of the title compound was initiated to establish the structures of the epoxides. A further interesting feature of the title compound was the fact that triterpenes, especially the pentacyclic ones, have been relatively seldom studied by X-ray methods.

The systematic absences in the diffraction pattern indicated the space group $P2_12_12_1$ (No. 19), and the cell parameters were obtained from a least-squares refinement of the angular settings of 25 reflections with a Syntex $P2_1$ (Fortran version) diffractometer. All reflections up to $2\theta = 45°$ were measured on the same diffractometer with graphite-monochromatized Mo $K\alpha$ radiation by the θ–2θ method and at a variable scan rate of 1 to 15° min^{-1}. Using the criterion $I > 2\sigma(I)$, 1787 reflections were considered as 'observed' and were

Table 1. *Final atomic coordinates for the nonhydrogen atoms* ($\times 10^4$)

	x	*y*	*z*
C(1)	10766 (4)	4377 (3)	7594 (1)
C(2)	11482 (5)	4307 (3)	8021 (1)
C(3)	10626 (5)	5159 (3)	8293 (1)
C(4)	8739 (5)	5025 (3)	8326 (1)
C(5)	8072 (4)	5037 (3)	7885 (1)
C(6)	6183 (4)	4998 (4)	7857 (1)
C(7)	5618 (4)	5387 (3)	7439 (1)
C(8)	6313 (4)	4627 (3)	7095 (1)
C(9)	8233 (4)	4543 (3)	7151 (1)
C(10)	8866 (4)	4178 (3)	7578 (1)
C(11)	9039 (4)	3874 (3)	6805 (1)
C(12)	8641 (4)	4413 (3)	6398 (1)
C(13)	6764 (4)	4477 (3)	6332 (1)
C(14)	5902 (4)	5213 (3)	6669 (1)
C(15)	3999 (4)	5211 (4)	6596 (1)
C(16)	3511 (5)	5589 (3)	6168 (1)
C(17)	4336 (5)	4807 (3)	5844 (1)
C(18)	6213 (4)	4823 (3)	5918 (1)
C(19)	7003 (5)	5520 (4)	5588 (1)
C(20)	8720 (6)	6031 (4)	5556 (1)
C(21)	5639 (6)	6020 (4)	5327 (1)
C(22)	4095 (5)	5318 (4)	5422 (1)
C(23)	8074 (6)	6132 (4)	8542 (1)
C(24)	8244 (6)	3945 (4)	8573 (1)
C(25)	8561 (6)	2873 (3)	7672 (1)
C(26)	5478 (5)	3404 (3)	7122 (1)
C(27)	6492 (5)	6489 (3)	6650 (1)
C(28)	3777 (5)	3539 (4)	5865 (1)
C(29)	8788 (8)	7304 (5)	5676 (2)
C(30)	9363 (6)	5894 (5)	5127 (1)
C(31)	12673 (5)	5653 (4)	8792 (1)
C(32)	13279 (7)	5398 (5)	9201 (1)
C(33)	1846 (6)	2445 (4)	5495 (1)
C(34)	160 (7)	2424 (5)	5317 (2)
O(35)	6999 (4)	4238 (2)	5578 (1)
O(36)	11318 (3)	5032 (2)	8699 (1)
O(37)	2146 (3)	3440 (2)	5695 (1)
O(38)	13301 (4)	6325 (3)	8564 (1)
O(39)	2806 (4)	1670 (3)	5470 (1)

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used in the subsequent calculations. Lorentz and polarization corrections were applied to the net intensities but no correction was made for absorption.

The structure was solved by direct methods using a locally enlarged version of the *MULTAN* program (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The atomic parameters were refined by full-matrix least-squares calculations. Three cycles of anisotropic refinement reduced R to 0·091. A Fourier difference map was then computed revealing the H atoms, and their contributions to the structure factors were included in the next three cycles of refinement using fixed isotropic temperature factors $B = 4$ Å^2 for the H atoms. In the next three cycles the H atoms were refined isotropically, and the alternate refinement of heavy and H atoms was repeated once. The final R index was 0·037 for all observed data (1787 reflections) and 0·035 for the 1765 reflections used in the refinement. The weighted R was 0·037 for all reflections using weights based on counting statistics [w =

Table 2. *Final atomic coordinates for the hydrogen atoms* ($\times 10^3$)

	x	y	z
H(1A)	1141 (4)	382 (3)	743 (1)
H(1B)	1107 (4)	510 (3)	747 (1)
H(2A)	1280 (4)	448 (3)	798 (1)
H(2B)	1143 (5)	349 (3)	815 (1)
H(3)	1092 (4)	596 (3)	819 (1)
H(5)	840 (3)	582 (2)	777 (7)
H(6A)	572 (4)	427 (3)	792 (1)
H(6B)	563 (4)	541 (3)	808 (1)
H(7A)	434 (4)	541 (3)	743 (1)
H(7B)	589 (4)	626 (2)	739 (1)
H(9)	863 (3)	532 (2)	712 (1)
H(11A)	1028 (3)	385 (2)	683 (1)
H(11B)	873 (3)	313 (2)	680 (1)
H(12A)	918 (4)	394 (2)	618 (1)
H(12B)	906 (3)	518 (2)	637 (1)
H(13)	635 (4)	361 (2)	637 (1)
H(15A)	350 (4)	439 (3)	664 (1)
H(15B)	348 (4)	571 (3)	678 (1)
H(16A)	221 (4)	545 (3)	614 (1)
H(16B)	383 (4)	646 (3)	611 (1)
H(20)	950 (5)	548 (3)	571 (1)
H(21A)	547 (5)	682 (3)	538 (1)
H(21B)	584 (5)	586 (3)	504 (1)
H(22A)	384 (5)	475 (3)	521 (1)
H(22B)	304 (4)	584 (3)	542 (1)
H(23A)	814 (5)	686 (3)	835 (1)
H(23B)	680 (5)	596 (3)	864 (1)
H(23C)	872 (5)	627 (3)	878 (1)
H(24A)	693 (5)	382 (3)	855 (1)
H(24B)	877 (4)	326 (3)	848 (1)
H(24C)	845 (5)	410 (3)	888 (1)
H(25A)	876 (5)	242 (3)	743 (1)
H(25B)	744 (4)	269 (3)	782 (1)
H(25C)	923 (5)	254 (3)	785 (1)
H(26A)	655 (4)	675 (3)	640 (1)
H(26B)	776 (5)	656 (3)	672 (1)
H(26C)	588 (5)	702 (3)	683 (1)
H(27A)	419 (5)	350 (3)	708 (1)
H(27B)	584 (5)	285 (3)	694 (1)
H(27C)	549 (5)	304 (4)	741 (1)
H(28A)	460 (4)	313 (3)	569 (1)
H(28B)	377 (5)	323 (3)	613 (1)
H(29A)	808 (7)	794 (4)	554 (1)
H(29B)	1007 (5)	753 (3)	564 (1)
H(29C)	821 (7)	766 (4)	593 (1)
H(30A)	924 (5)	511 (3)	504 (1)
H(30B)	1072 (7)	608 (5)	509 (2)
H(30C)	874 (5)	646 (3)	493 (1)
H(32A)	1423 (7)	503 (5)	919 (1)
H(32B)	1356 (7)	615 (4)	932 (1)
H(32C)	1258 (5)	496 (4)	937 (1)
H(34A)	−74 (7)	259 (4)	552 (1)
H(34B)	−13 (7)	154 (5)	521 (2)
H(34C)	4 (6)	295 (4)	512 (1)

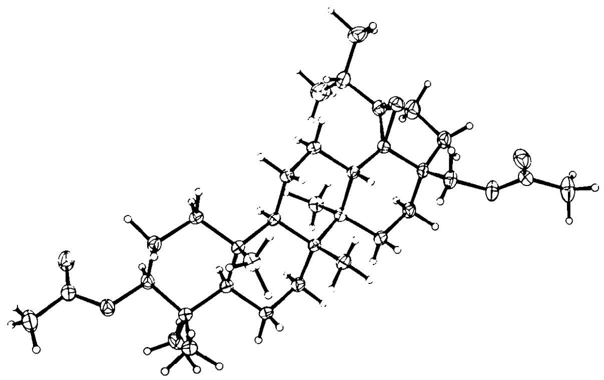

Fig. 1. A perspective view of the molecule. The thermal ellipsoids of the non-H atoms are scaled to include 30% probability.

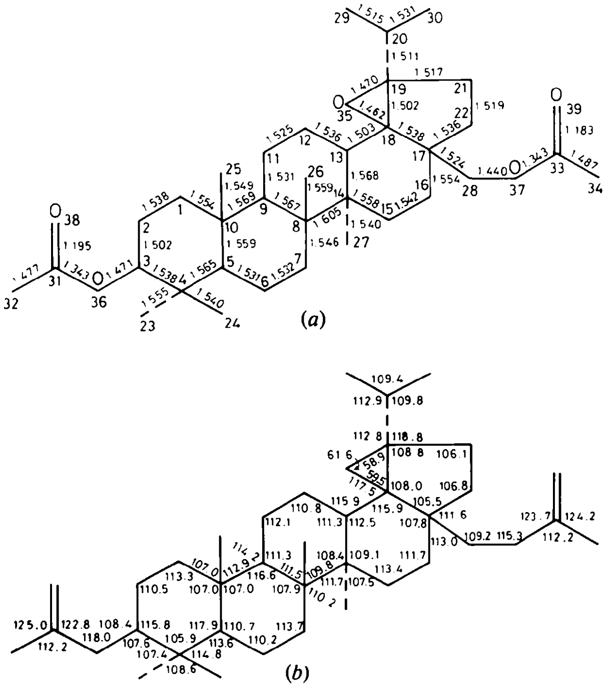

Fig. 2. Atomic numbering and intramolecular geometry of the molecule. (a) Bond distances (Å) and (b) angles (°).

$1/\sigma^2(F_o^2)$]. The final positional parameters are listed for C and O in Table 1 and for H in Table 2.*

Discussion. Fig. 1 shows a perspective view of the molecule. The atomic numbering scheme is given in Fig. 2 which also shows the bond lengths between nonhydrogen atoms of the molecule as well as the corresponding angles. The standard deviations in the distances and angles involving nonhydrogen atoms are in the ranges 0·004–0·007 Å and 0·3–0·4°, respectively.

In addition to the epoxy ring, the molecule consists of four six-membered rings, all in the chair conformation, and of one five-membered ring. The average C—C distance within the five *trans* fused rings is 1·54 Å or close to the normal value for sp^3 hybridized C atoms. The 54 C—H bonds are in the range 0·88–1·18 Å; the mean length is 1·00 Å.

The structure determination establishes the following stereochemistry: peracid epoxidation at the C(18) double bond produces the β-epoxide and hence the isomeric compound obtained by ozone treatment has the α-epoxide structure. The absolute configuration of the molecule was not determined by X-ray crystallographic methods but the chemical evidence available indicates a β-oxygen at C(3).

The present structure may be compared to that of a closely related lupane derivative, 3β-acetoxy-20-hydroxylupane, for which the crystal and molecular structure has been determined from diffractometer data (Watson, Ting & Dominguez, 1972). The conformations of both triterpenes are the same but there seem to be some differences in the bond distances and angles; this is partly due to the epoxy function which brings strain to the *D* and *E* rings. There are differences in other rings which may also be significant. On the other hand, some of the extreme values in both compounds are consistent; for instance the C(8)—C(14) bond length (1·605 Å), which deviates most from the mean in the present structure, is almost the same (1·613 Å) in the 3β-acetoxy-20-hydroxylupane molecule.

In order to study in more detail the molecular structure and the effect of substituents thereon, accurate additional data would be useful; these will soon be available for a related compound 3β-acetoxy-13α,18α-epoxylupane (Hiltunen, 1979).

We thank Dr E. Suokas for suggesting the problem and providing the crystals.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34322 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Conformational investigation of *tert*-butoxycarbonylhexa(L-valyl) methyl ester by X-ray techniques.

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Abstract

Observations of extended peptide chains, whose direction is perpendicular to the fiber axis (cross-β structure), have hitherto been confined to fibrous proteins and to some synthetic polydisperse polypeptides of rather low molecular weight. This structure has now been found in some monodisperse linear homo-oligopeptides with aliphatic hydrocarbon side chains. X-ray diffraction photographs of *tert*-butoxycarbonylhexa(L-valyl) methyl ester, $C_{36}H_{66}N_6O_9$, show the characteristic reflections of this form. In addition, the good orientation of suitably prepared specimens has

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