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The Crystal and Molecular Structures of the Triclinic and Orthorhombic Forms of 18-α(*H*)-Oleanane, $C_{30}H_{52}$

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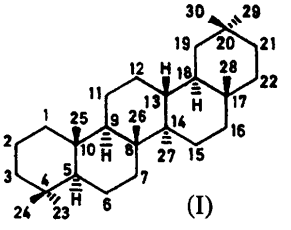
An unknown triterpane, extracted from a Nigerian crude petroleum, has been identified as 18-α(*H*)-oleanane by the determination of its crystal structures. The compound crystallizes in two forms. The structure of the triclinic form [space group *P*1, $Z = 1$, $a = 7{\cdot}275$ (7), $b = 14{\cdot}88$ (1), $c = 6{\cdot}676$ (7) Å, $\alpha = 97{\cdot}9$ (1), $\beta = 63{\cdot}9$ (1), $\gamma = 96{\cdot}5$ (1)°] was refined to $R = 0{\cdot}136$ for 963 counter reflexions. The structure of the orthorhombic form [space group $P2_12_12_1$, $Z = 8$, $a = 20{\cdot}44$ (2), $b = 20{\cdot}90$ (2), $c = 12{\cdot}20$ (2) Å] was refined to $R = 0{\cdot}142$ for 2160 counter reflexions. Both structures yielded the same molecule which consists of five *trans*-fused six-membered rings with geminal dimethyl groups at C(4) and C(20), and four other methyl groups at C(10), C(8), C(14) and C(17). There is evidence in the electron density maps to suggest that the triclinic form is an artefact arising possibly from an impurity but more likely from a disorder of the packing.

Introduction

The structures of three unknown triterpanes, *E*, *H* and *D* (Smith, 1970, 1974*a*,*b*) have been reported. Triterpane *F*, another in the series of pentacyclic hydrocarbons extracted from a Nigerian crude petroleum (Hills & Whitehead, 1966), was examined by mass spectrometer and NMR methods and shown to have the formula $C_{30}H_{52}$ with eight methyl groups. It crystallizes in an orthorhombic form, which has been briefly reported (Smith, Fowell & Melsom, 1970), and a triclinic form. The structure determination of both crystals yielded the same molecule, 18-α(*H*)-oleanane (I).



(I)

It is unusual to find more than one crystal form of such molecules but there is evidence to suggest that the triclinic form might be an artefact, brought about possibly by an impurity, although the purity by weight as determined by high-resolution capillary-column GLC on different stationary bases at different temperatures was better than 98%. A more likely explanation is disordered packing occurring during crystallization. The orthorhombic crystals were well formed laths or needles while the triclinic crystals were irregular plates. Crystals of the latter frequently showed strongly streaked spots and subsequent attempts to improve crystal quality by recrystallization resulted in an increased proportion of the orthorhombic form at the expense of the triclinic.

Crystal data

The plate normal in the triclinic form was taken as b^* and the needle axis in the orthorhombic form as [001]. Cell constants were obtained from zero-layer Weissenberg photographs taken about all three axes of each crystal form, by extrapolation of successive orders of the principal rows, with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å).

Triterpane *F*, $C_{30}H_{52}$, $M_r = 412{\cdot}416$, accurate mass (molecular ion) by mass spectrometry = 412·408, μ(Mo $K\alpha$) = 0·65 cm^{-1}; the optic sign of both crystals is positive.

Triclinic

$a = 7{\cdot}275$ (7), $b = 14{\cdot}88$ (1), $c = 6{\cdot}676$ (7) Å, $\alpha = 97{\cdot}9$ (1), $\beta = 63{\cdot}9$ (1), $\gamma = 96{\cdot}5$ (1)°, $U = 641{\cdot}8$ Å^3, $D_x = 1{\cdot}067$, $D_m = 1{\cdot}070$ (2) g cm^{-3}, $F(000) = 232$, space group *P*1, $Z = 1$.

Orthorhombic

$a = 20{\cdot}44$ (2), $b = 20{\cdot}90$ (2), $c = 12{\cdot}20$ (2) Å, $U = 5211{\cdot}8$ Å^3, $D_x = 1{\cdot}051$, $D_m = 1{\cdot}051$ (2) g cm^{-3}, $F(000) = 1856$, space group $P2_12_12_1$, $Z = 8$. The densities for both forms were measured by flotation in aqueous KI.

Experimental

The intensities were collected at room temperature with Mo $K\alpha$ radiation on a Pailred automatic diffractometer fitted with a graphite monochromator, by courtesy of Dr G. J. Bullen (Univ. of Essex). For the triclinic form, data were collected from a crystal 0·2 × 0·2 × 0·05 mm mounted about **a** for the layers $h = 0$–7. For the orthorhombic form, a needle crystal 0·15 × 0·15 × 0·3 mm mounted about **c** was used for the layers $l = 0$–12. For both crystals additional Weissenberg films were taken with Mo Kα radiation to provide supplementary data. Reflexions whose net intensities were $<3\sigma$ above background were taken as unobserved and, after Lp correction, were given an F value corresponding to $\frac{1}{2}F$(min) for the layer in which they occurred. No absorption correction was made. Approximate scale and overall temperature factors were obtained from a Wilson plot. The numbers of reflexions recorded were: triclinic: total 1332, observed 963; orthorhombic: total 3215, observed 2610.

Structure determination

Triclinic

There was a strong similarity between the intensity distribution of the 0kl of F and the $h0l$ reflexions of E which played an important part in recognition of the ring skeleton. The sharpened Patterson map showed the molecular orientation clearly, so that the positions of the Patterson peaks could be taken as atomic sites. Two trials were needed to establish that all five rings were all-chair all-*trans* six-membered rings, and two further trials to fix the positions of the eight methyl groups.

Orthorhombic

The structure was solved by direct methods (Karle & Karle, 1966) based on programs written by Brenner & Gum (1968), since the cell dimensions gave little clue to the molecular orientation while the Patterson synthesis was uninterpretable except for identifying the shortest C–C vectors. The starting reflexions were 0,12,7, 012 and 930 plus four other starting reflexions which included two real 0gg and two complex types. The tangent formula was used to calculate 64 sets of phase combinations and expand the data set to 190 reflexions with $E \geq 1{\cdot}6$. The set which gave the lowest residual yielded the correct structure and the resulting E map revealed 52 of the 60 atoms, 26 in each molecule. An F_o map phased upon these 52 atoms showed the remaining atoms.

Refinement

The block-diagonal refinement of both structures was carried out with the NRC program system (Ahmed, Hall, Pippy & Huber, 1966). Scattering factors for C and H were taken from *International Tables for X-ray Crystallography* (1962).

Triclinic

Isotropic refinement of the C atoms reduced R to 0·198 for the observed reflexions only. The positions of those H atoms fixed by geometry were calculated, based on C–H = 1·08 Å. The methyl H atom positions were extracted from difference maps. The inclusion of their fixed contribution to the structure factors reduced R to 0·179, with weights $w^{-1} = 1 + (F - 5)^2/15^2$. Attempts to refine beyond this point resulted in increasing distortion of the molecular geometry and unlikely temperature factors, which were attributed to the limited amount of data. A scan of the unobserved reflexions revealed that only 12% had $F_o > F_c$, and that if the unobserved reflexions were given $F_o = F$(min) instead of $\frac{1}{2}F$(min) then this proportion would be raised to 42%. Accepting this new criterion for the unobserved reflexions and including them in the refinement only if $\Delta F/F \leq 2{\cdot}0$ reduced R to only 0·178 but the number of reflexions used rose to 1305. As a result, the molecular geometry and the temperature factors

Table 1. *Fractional coordinates* (×10⁴) *for* C *atoms of the triclinic structure*

E.s.d.'s are in parentheses and refer to the last decimal places.

	x	y	z
C(1)	2955 (29)	7588 (12)	8762 (30)
C(2)	2773 (33)	8650 (14)	9560 (32)
C(3)	4777 (27)	9025 (13)	9736 (31)
C(4)	6758 (21)	8861 (9)	7646 (25)
C(5)	6706 (22)	7781 (10)	6794 (24)
C(6)	8729 (29)	7572 (12)	4725 (34)
C(7)	8904 (19)	6478 (11)	4633 (27)
C(8)	7160 (23)	5950 (11)	4387 (25)
C(9)	5076 (22)	6294 (9)	6313 (25)
C(10)	4826 (21)	7327 (9)	6564 (22)
C(11)	3184 (30)	5728 (11)	6287 (41)
C(12)	3356 (26)	4697 (13)	6405 (30)
C(13)	5318 (24)	4303 (11)	4474 (27)
C(14)	7230 (25)	4906 (10)	4680 (27)
C(15)	9209 (24)	4466 (12)	2846 (31)
C(16)	9216 (30)	3491 (17)	2862 (37)
C(17)	7406 (20)	2923 (10)	2689 (25)
C(18)	5535 (22)	3294 (10)	4618 (24)
C(19)	3534 (27)	2699 (12)	4673 (35)
C(20)	3591 (25)	1724 (15)	4854 (33)
C(21)	5637 (36)	1369 (14)	3043 (35)
C(22)	7516 (22)	1866 (10)	3005 (27)
C(23)	6978 (34)	9446 (14)	5826 (39)
C(24)	8451 (36)	9089 (12)	8223 (38)
C(25)	4442 (27)	7651 (10)	4751 (29)
C(26)	7163 (24)	5968 (9)	2168 (26)
C(27)	7257 (22)	4804 (11)	6986 (27)
C(28)	7551 (26)	3031 (12)	445 (29)
C(29)	1741 (33)	1182 (13)	4436 (4)
C(30)	3333 (40)	1540 (16)	7198 (38)

improved. A limited anisotropic refinement, with a 9 × 9 matrix for C atoms only, reduced R to 0·136 for the observed reflexions and 0·155 for all reflexions, with weights $w^{-1} = 1 + (F - 5)^2/30^2$. Additional refinement gave no reduction in R and produced an increasing number of meaningless temperature factors. Throughout the refinement optimum layer scale factors were calculated (Eichhorn, 1956).

The electron density and difference maps also showed some residual peaks, to be discussed later, in positions not associated with the molecule and attempts to include them in the refinement, as fractionally occupied C atom sites, failed. The final coordinates for the C atoms are given in Table 1.*

Orthorhombic

With observed reflexions only, isotropic refinement of C atoms reduced R to 0·193. Following the inclusion of the 56 H atoms fixed by geometry and the 48 methyl H positions extracted from difference maps, R was reduced to 0·174. Subsequent Fourier syntheses showed that the H atoms associated with the methyl C(24), C(25), C(26), C(54), C(55) and C(56) were in two sets of positions which were given 50% occupancy factors. Isotropic refinement of C atoms continued until R was 0·154. Anisotropic refinement, for C atoms only, finally reduced R to 0·142 for all observed reflexions. The weights were $w^{-1} = F/30$ for $F \leq 30$ and $w^{-1} = 30/F$ for $F > 30$. Optimum layer scale factors were calculated at intervals as for the triclinic structure and the 002 reflexion was excluded from the refinement because of extinction. Final parameters of the C atoms are listed in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, and H atom parameters for both forms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33448 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion of the structures

The numbering system is the same in both structures: C(1) to C(30), with a parallel numbering C(31) to C(60) for the second molecule of the orthorhombic

* See deposition footnote.

Table 2. *Fractional coordinates* (×10⁴) *for* C *atoms of the orthorhombic structure*

E.s.d.'s are in parentheses and refer to the last decimal places.

	x	y	z		x	y	z
Molecule 1				Molecule 2			
C(1)	1346 (7)	5405 (6)	4477 (13)	C(31)	4012 (6)	7773 (6)	4405 (11)
C(2)	767 (8)	5893 (7)	4540 (13)	C(32)	3489 (7)	8300 (7)	4298 (12)
C(3)	154 (7)	5578 (6)	4838 (12)	C(33)	2820 (7)	8047 (7)	4429 (13)
C(4)	174 (6)	5205 (6)	5915 (11)	C(34)	2697 (6)	7679 (6)	5512 (13)
C(5)	773 (6)	4721 (5)	5864 (10)	C(35)	3244 (6)	7188 (7)	5631 (11)
C(6)	844 (7)	4297 (6)	6876 (11)	C(36)	3186 (6)	6734 (7)	6601 (13)
C(7)	1282 (6)	3724 (7)	6588 (11)	C(37)	3598 (6)	6113 (7)	6482 (11)
C(8)	1969 (5)	3913 (6)	6199 (10)	C(38)	4330 (6)	6253 (6)	6285 (11)
C(9)	1899 (6)	4424 (6)	5287 (10)	C(39)	4408 (6)	6784 (6)	5400 (11)
C(10)	1435 (7)	5007 (6)	5522 (10)	C(40)	3971 (6)	7396 (6)	5496 (12)
C(11)	2562 (6)	4607 (7)	4810 (12)	C(41)	5144 (6)	6935 (7)	5172 (11)
C(12)	2947 (6)	4046 (6)	4424 (11)	C(42)	5527 (7)	6317 (7)	4862 (12)
C(13)	3033 (6)	3499 (6)	5291 (10)	C(43)	5438 (6)	5787 (6)	5730 (10)
C(14)	2326 (6)	3320 (5)	5721 (9)	C(44)	4710 (5)	5613 (6)	5907 (10)
C(15)	2419 (7)	2783 (6)	6572 (11)	C(45)	4642 (6)	5077 (6)	6758 (10)
C(16)	2866 (8)	2211 (7)	6229 (13)	C(46)	5093 (7)	4500 (7)	6509 (13)
C(17)	3559 (7)	2465 (7)	5853 (11)	C(47)	5808 (6)	4682 (6)	6366 (12)
C(18)	3461 (6)	2930 (6)	4932 (11)	C(48)	5842 (6)	5178 (7)	5452 (10)
C(19)	4107 (6)	3152 (7)	4426 (12)	C(49)	6579 (7)	5339 (7)	5184 (12)
C(20)	4535 (6)	2578 (7)	4012 (12)	C(50)	6989 (7)	4747 (7)	4878 (13)
C(21)	4602 (7)	2070 (7)	4892 (12)	C(51)	6897 (7)	4205 (8)	5706 (14)
C(22)	3933 (8)	1883 (7)	5390 (13)	C(52)	6176 (7)	4077 (8)	5998 (14)
C(23)	−466 (7)	4798 (8)	5992 (16)	C(53)	2044 (7)	7321 (7)	5342 (14)
C(24)	192 (8)	5663 (8)	6921 (13)	C(54)	2637 (8)	8138 (7)	6508 (13)
C(25)	1725 (6)	5478 (7)	6422 (13)	C(55)	4214 (7)	7855 (6)	6427 (13)
C(26)	2359 (7)	4175 (7)	7240 (11)	C(56)	4614 (7)	6481 (7)	7426 (12)
C(27)	1926 (6)	3014 (6)	4765 (10)	C(57)	4329 (5)	5371 (6)	4818 (11)
C(28)	3935 (7)	2738 (8)	6887 (12)	C(58)	6087 (7)	4908 (8)	7501 (12)
C(29)	5210 (8)	2821 (7)	3722 (15)	C(59)	7712 (7)	4929 (8)	4875 (16)
C(30)	4240 (9)	2295 (9)	2984 (14)	C(60)	6796 (10)	4507 (9)	3731 (15)

structure. The bond-distance and bond-angle tables, however, refer only to C(1) to C(30).

These structure determinations have shown that both crystal forms contain the molecule 18-α(*H*)-oleanane which possesses five fused six-membered rings in the *trans*-chair configuration, with geminal dimethyl groups at C(4) and C(20) plus four additional methyl groups at C(10), C(8), C(14) and C(17).

In the triclinic form, the relatively small amount of data limited the refinement to a high *R* and required the inclusion of most of the unobserved reflexions, inside the observable limit, for a stable result to be obtained. There were several spurious peaks in the electron density maps, not associated with the molecule itself. Most of these peaks had heights of 1·5–1·7 e Å^{-3} and occurred at the centres of the *A*, *B*, *C* and *D* rings and between C(1)—C(11) and C(7)—C(15), while other less prominent peaks were in a plane nearly parallel to the main molecule. Attempts to include them in the refinement failed. It is possible that these peaks arise from an impurity, although the degree of purity by GLC makes this unlikely. A more probable cause is that, as the molecule has regular features, it could occupy more than one position or orientation in the unit cell, with some atoms of both positions coincident. For example, if C(1), C(5), C(7), C(9) and C(14) are taken as coincident sites, then together with the extra peak positions it becomes possible to construct a four-ring skeleton in a displaced position. Many of the triclinic crystals that were examined exhibited streaky spots suggesting the presence of some kind of disorder, although the crystal selected for intensity measurement was chosen because it did not show the effect markedly. The $N(z)$ test was also remarkable in that it gave an almost perfect centric distribution of intensities. It has already been noted that repeated crystallization reduced the amount of triclinic crystals relative to the orthorhombic form. Therefore it seems as though the triclinic form is an artefact induced by crystallization conditions only, and whilst the molecular geometry is less affected, the disorder has resulted in somewhat unrealistic temperature factors (Fig. 1).

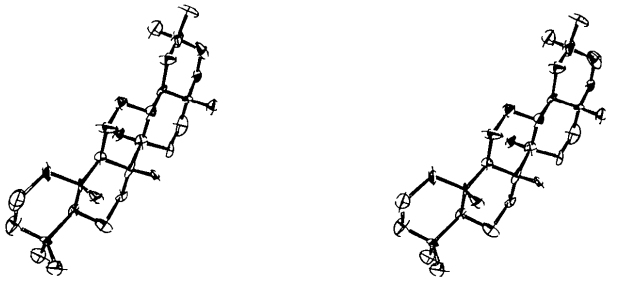


Fig. 1. Stereoscopic view of triterpane *F*, triclinic structure, drawn by *ORTEP* (Johnson, 1965). Vibration ellipsoids are scaled to 50% probability.

The packing in the triclinic structure (Fig. 2) is similar to triterpanes *E*, *H* and *D*, being in the class *a*111 (Bernal, Crowfoot & Fankuchen, 1940).

The orthorhombic form has a different form of packing. The thermal-ellipsoid plot is shown in Fig. 3 and the packing diagram of half the unit-cell contents viewed down **c** in Fig. 4. The molecules lie roughly parallel to each other with an angle of 8° between the mean planes of all five rings and diagonally across the *ab* face. These mean planes make angles of 43·2 and 35·4° with (001) respectively. There are only four normal van der Waals distances: C(6)—C(57) = 3·69, C(12)—C(25) = 3·85 and C(58)—C(59) = 3·81 Å for the operations (x,y,z) and $(\frac{1}{2}-x,\ \bar{y},\ \frac{1}{2}+z)$ and C(21)—C(56) = 3·85 Å for the operations (x,y,z) and $(\bar{x},\ \frac{1}{2}+y,\ \frac{1}{2}-z)$. There are seven distances in the range 3·9–4·0 Å and eleven others 4·0–4·1 Å. This loose packing is in agreement with the 2% difference in density of the two crystal forms and presumably allows the methyl H atoms of C(24), C(25), C(26), C(54), C(55) and C(56) to adopt two orientations. The steric effect of these H atoms still remains and shows itself in the angles between the mean planes of each of the five rings (Table 5).

The bond angles are listed in Table 3 and bond distances in Table 4. The mean bond angle for the triclinic form is 110·5 (3·4)° with all angles within 2σ; the values for the orthorhombic molecules 1 and 2 are 110·9 (2·8) and 110·9 (2·9)° respectively. The mean C—C distance in the triclinic form is 1·544 (53) Å and, although all distances lie within 2σ of the mean, lack of sufficient data in the refinement has produced large individual standard deviations which preclude a meaningful comparison. The results for the bond distances of the two independent molecules of the orthorhombic structure are better, though here again

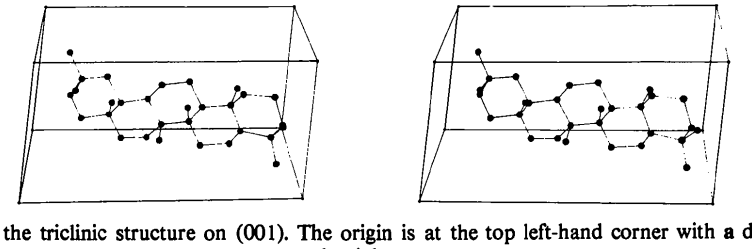


Fig. 2. Stereoscopic view of the triclinic structure on (001). The origin is at the top left-hand corner with **a** down and **b** horizontal to the right.

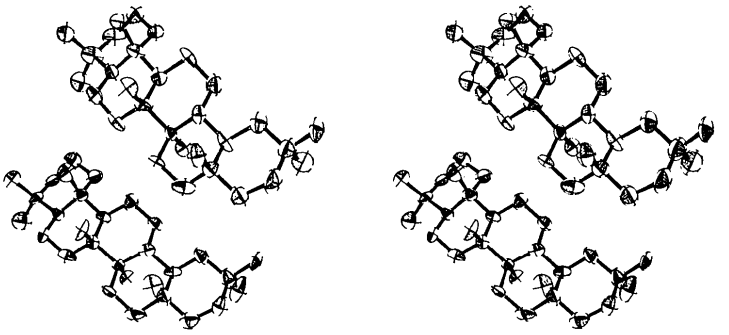


Fig. 3. Stereoscopic view of the pair of independent molecules, orthorhombic structure, drawn by *ORTEP*. Vibration ellipsoids are scaled to 50% probability.

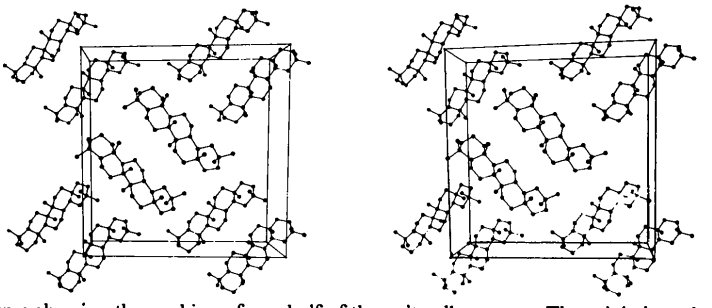


Fig. 4. Stereoscopic view down **c** showing the packing of one-half of the unit-cell contents. The origin is at the bottom left-hand corner with **a** horizontal and **b** vertical.

Table 3. *Bond angles* (°) *for both structures*

E.s.d.'s are in parentheses. For numbering see (I).

	Triclinic	Orthorhombic Molecule 1	Orthorhombic Molecule 2		Triclinic	Orthorhombic Molecule 1	Orthorhombic Molecule 2
C(2)–C(1)–C(10)	115·9 (1·5)	113·7 (1·1)	113·5 (1·1)	C(11)–C(12)–C(13)	112·8 (1·6)	114·9 (1·0)	111·7 (1·1)
C(1)–C(2)–C(3)	108·1 (1·7)	111·5 (1·2)	112·2 (1·2)	C(12)–C(13)–C(14)	106·2 (1·4)	107·0 (0·9)	112·2 (1·0)
C(2)–C(3)–C(4)	116·3 (1·6)	114·9 (1·2)	114·8 (1·2)	C(12)–C(13)–C(18)	113·2 (1·4)	115·8 (1·0)	112·0 (1·1)
C(3)–C(4)–C(5)	107·0 (1·3)	108·1 (1·0)	107·3 (1·1)	C(14)–C(13)–C(18)	108·9 (1·3)	115·5 (1·0)	110·4 (1·0)
C(3)–C(4)–C(23)	111·0 (1·5)	107·9 (1·1)	105·4 (1·1)	C(8)–C(14)–C(13)	111·0 (1·3)	111·5 (0·9)	108·0 (0·9)
C(3)–C(4)–C(24)	108·7 (1·5)	111·4 (1·1)	111·9 (1·2)	C(8)–C(14)–C(15)	112·5 (1·4)	112·7 (0·9)	111·5 (0·9)
C(5)–C(4)–C(23)	111·2 (1·4)	107·5 (1·0)	108·7 (1·1)	C(8)–C(14)–C(27)	111·1 (1·3)	111·2 (0·9)	108·2 (0·9)
C(5)–C(4)–C(24)	109·7 (1·4)	113·9 (1·0)	113·6 (1·2)	C(13)–C(14)–C(15)	106·3 (1·3)	106·4 (0·9)	110·7 (1·0)
C(23)–C(4)–C(24)	109·2 (1·6)	107·9 (1·1)	109·6 (1·2)	C(13)–C(14)–C(27)	110·2 (1·3)	109·1 (0·9)	111·0 (1·0)
C(4)–C(5)–C(6)	109·1 (1·3)	114·2 (1·0)	116·0 (1·1)	C(15)–C(14)–C(27)	105·4 (1·4)	105·7 (0·9)	107·5 (1·0)
C(4)–C(5)–C(10)	119·9 (1·3)	116·2 (1·0)	120·1 (1·1)	C(14)–C(15)–C(16)	114·5 (1·7)	116·7 (1·1)	112·5 (1·0)
C(6)–C(5)–C(10)	113·5 (1·4)	111·2 (1·0)	109·3 (1·1)	C(15)–C(16)–C(17)	116·2 (1·8)	110·3 (1·1)	113·5 (1·1)
C(5)–C(6)–C(7)	104·4 (1·4)	108·8 (1·0)	114·0 (1·1)	C(16)–C(17)–C(18)	105·5 (1·4)	108·3 (1·1)	107·4 (1·1)
C(6)–C(7)–C(8)	111·6 (1·4)	113·8 (1·0)	112·5 (1·1)	C(16)–C(17)–C(22)	110·0 (1·4)	106·6 (1·1)	107·4 (1·2)
C(7)–C(8)–C(9)	109·9 (1·3)	108·3 (0·9)	110·0 (1·0)	C(16)–C(17)–C(28)	106·0 (1·6)	108·9 (1·1)	108·9 (1·1)
C(7)–C(8)–C(14)	109·3 (1·3)	110·0 (0·9)	110·8 (1·0)	C(18)–C(17)–C(22)	108·4 (1·2)	107·7 (1·1)	108·9 (1·1)
C(7)–C(8)–C(26)	114·0 (1·4)	107·5 (1·0)	106·0 (1·0)	C(18)–C(17)–C(28)	114·5 (1·4)	115·4 (1·2)	115·1 (1·1)
C(9)–C(8)–C(14)	106·7 (1·3)	108·9 (0·9)	110·1 (1·0)	C(22)–C(17)–C(28)	112·3 (1·3)	109·6 (1·2)	109·1 (1·1)
C(9)–C(8)–C(26)	110·0 (1·3)	112·3 (0·9)	110·9 (1·0)	C(13)–C18)–C(17)	112·0 (1·3)	111·3 (1·0)	111·9 (1·1)
C(14)–C(8)–C(26)	106·6 (1·3)	109·8 (0·9)	109·0 (1·0)	C(13)–C(18)–C(19)	109·6 (1·3)	111·7 (1·0)	112·2 (1·1)
C(8)–C(9)–C(10)	115·5 (1·3)	117·4 (1·0)	118·2 (1·0)	C(17)–C(18)–C(19)	109·4 (1·3)	112·5 (1·1)	109·9 (1·1)
C(8)–C(9)–C(11)	113·1 (1·4)	111·5 (1·0)	111·5 (1·0)	C(18)–C(19)–C(20)	113·4 (1·6)	112·3 (1·1)	113·4 (1·2)
C(10)–C(9)–C(11)	112·4 (1·4)	114·3 (1·0)	113·5 (1·0)	C(19)–C(20)–C(21)	109·3 (1·7)	111·0 (1·1)	111·7 (1·2)
C(1)–C(10)–C(5)	107·1 (1·3)	109·4 (1·0)	106·6 (1·0)	C(19)–C(20)–C(29)	108·3 (1·7)	109·1 (1·2)	109·1 (1·2)
C(1)–C(10)–C(9)	109·6 (1·3)	109·9 (1·0)	108·8 (1·0)	C(19)–C(20)–C(30)	112·7 (1·8)	110·1 (1·2)	110·1 (1·3)
C(1)–C(10)–C(25)	105·3 (1·3)	106·4 (1·1)	107·0 (1·0)	C(21)–C(20)–C(29)	109·1 (1·7)	108·5 (1·2)	107·8 (1·3)
C(5)–C(10)–C(9)	105·7 (1·2)	106·2 (1·0)	109·0 (1·0)	C(21)–C(20)–C(30)	109·5 (1·8)	110·5 (1·3)	109·1 (1·3)
C(5)–C(10)–C(25)	114·3 (1·3)	112·5 (1·0)	113·4 (1·1)	C(29)–C(20)–C(30)	107·9 (1·8)	107·5 (1·3)	109·1 (1·3)
C(9)–C(10)–C(25)	114·6 (1·3)	112·4 (1·0)	111·9 (1·1)	C(20)–C(21)–C(22)	116·4 (1·8)	112·0 (1·2)	113·5 (1·2)
C(9)–C(11)–C(12)	110·7 (1·6)	113·1 (1·1)	111·1 (1·1)	C(17)–C(22)–C(21)	107·6 (1·4)	112·5 (1·2)	113·2 (1·3)

Table 4. *Interatomic distances* (Å)

E.s.d.'s in parentheses refer to the last two decimal places. For numbering see (I).

	Triclinic	Orthorhombic Molecule 1	Orthorhombic Molecule 2		Triclinic	Orthorhombic Molecule 1	Orthorhombic Molecule 2
C(1)–C(2)	1·598 (27)	1·564 (20)	1·541 (19)	C(11)–C(12)	1·569 (26)	1·490 (18)	1·557 (20)
C(1)–C(10)	1·536 (24)	1·534 (20)	1·549 (13)	C(12)–C(13)	1·550 (26)	1·567 (18)	1·543 (20)
C(2)–C(3)	1·549 (33)	1·462 (21)	1·475 (20)	C(13)–C(14)	1·616 (26)	1·583 (17)	1·546 (16)
C(3)–C(4)	1·516 (25)	1·528 (19)	1·548 (22)	C(13)–C(18)	1·548 (22)	1·540 (17)	1·555 (18)
C(4)–C(5)	1·632 (20)	1·590 (17)	1·524 (18)	C(14)–C(15)	1·562 (26)	1·541 (17)	1·534 (17)
C(4)–C(23)	1·533 (27)	1·564 (19)	1·546 (19)	C(14)–C(27)	1·576 (23)	1·561 (16)	1·563 (18)
C(4)–C(24)	1·438 (33)	1·557 (20)	1·554 (22)	C(15)–C(16)	1·453 (31)	1·562 (20)	1·548 (18)
C(5)–C(6)	1·538 (27)	1·527 (18)	1·521 (20)	C(16)–C(17)	1·523 (29)	1·581 (21)	1·520 (19)
C(5)–C(10)	1·516 (24)	1·536 (18)	1·557 (18)	C(17)–C(18)	1·499 (22)	1·499 (19)	1·524 (19)
C(6)–C(7)	1·637 (24)	1·535 (19)	1·553 (20)	C(17)–C(22)	1·630 (21)	1·543 (21)	1·539 (21)
C(7)–C(8)	1·476 (24)	1·534 (17)	1·534 (18)	C(17)–C(28)	1·485 (23)	1·584 (21)	1·571 (20)
C(8)–C(9)	1·578 (23)	1·549 (16)	1·558 (18)	C(18)–C(19)	1·606 (27)	1·529 (18)	1·579 (18)
C(8)–C(14)	1·603 (23)	1·550 (16)	1·613 (17)	C(19)–C(20)	1·480 (28)	1·568 (20)	1·540 (21)
C(8)–C(26)	1·484 (22)	1·597 (18)	1·582 (19)	C(20)–C(21)	1·541 (32)	1·517 (21)	1·530 (23)
C(9)–C(10)	1·546 (20)	1·570 (17)	1·563 (18)	C(20)–C(29)	1·601 (33)	1·514 (21)	1·528 (20)
C(9)–C(11)	1·536 (28)	1·523 (17)	1·562 (17)	C(20)–C(30)	1·551 (31)	1·512 (23)	1·538 (24)
C(10)–C(25)	1·505 (24)	1·590 (19)	1·569 (20)	C(21)–C(22)	1·471 (31)	1·547 (21)	1·540 (21)

Table 5. *Angles* (°) *between the mean planes of the rings for both structures*

Rings	Triclinic	Orthorhombic Molecule 1	Orthorhombic Molecule 2
$A \wedge B$	15·5	12·1	15·6
$B \wedge C$	6·8	10·5	9·1
$C \wedge D$	2·9	6·2	5·2
$D \wedge E$	7·1	5·3	5·8

the reduced amount of data has resulted in individual standard deviations that are larger than those obtained for triterpanes *E*, *H* and *D*. The mean C–C distance is 1·546 (30) for molecule 1 and 1·547 (23) Å for molecule 2, and there is a close parallel between equivalent bonds in each molecule. Molecule 1 has only one bond outside the 2σ limit while molecule 2 has two such distances which also fall outside the 3σ limit. The C(2)–C(3) distance, in molecules 1 and 2, is 1·462 and 1·475 Å and is also a short distance in triterpane *H* but not in triterpane *D*. The distance C(8)–C(14) is also of some interest as the individual values differ from their mean of 1·582 Å by only about 1σ. In many triterpenoid structures this distance often exceeds 1·62 Å but, as was reported in the structures of compounds *H* and *D*, the lengthening of this bond is more likely to be attributable to the strain induced by a *cis D/E* ring junction than by the steric effect of the methyl groups at C(4), C(10) and C(8) which manifests itself chiefly in twisting the mean planes of the *A*, *B* and *C* rings.

The identification of triterpane *F* as 18-α(*H*)-oleanane and its significance to the origin of petroleum is discussed in detail by Whitehead (1973*a*,*b*). It is generally considered that 18-α(*H*)-oleanane is a key intermediate in the biosynthetic pathway between squalene and the lupane, ursane and oleanane triterpenoids. However, an apparent reversal of this sequence can occur since it is known that natural ursane, oleanane and friedelane triterpenoids can be rearranged under acid conditions back to the fundamental 18-α(*H*)-oleanane system. In particular, certain lupane derivatives can be rearranged with only traces of acid to give oxyallobetul-2-ene (Fig. 5), which has been identified in Kuwait crude oil (Barton, Carruthers & Overton, 1956). The stereochemistry of the OH group at C(3) in oxyallobetulin could be a critical feature in determining the final form of the molecule. For instance, during maturation, if the OH group is in the α position, the removal of the OH under acid conditions would permit a *trans* migration of C(23) to C(3) and permit spiranization of rings *A* and *B*, *via* a carbonium ion involving C(1), C(5) and C(10), leaving C(25) in the unnatural α position. The end product is then triterpane *E*, a modified 18-α(*H*)-oleanane. On the other hand, if the OH group at C(3) is in the β configuration then this spiranization of rings *A* and *B* does not occur upon its loss; instead a double bond at

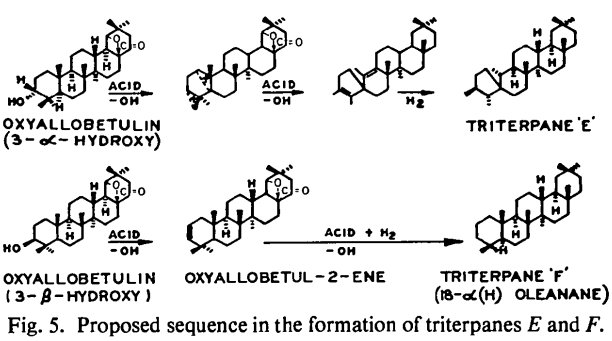


Fig. 5. Proposed sequence in the formation of triterpanes *E* and *F*.

C(2) is induced in oxyallobetul-2-ene and, following the removal of the lactone bridge across ring *E*, the final hydrogenated product is triterpane *F*. The mechanism is paralleled by the loss of an equatorial β-OH from gammaceran-3β-ol which after hydrogenation gives gammacerane which has been identified in a Green River shale oil (Hills, Whitehead, Anders, Cummins & Robinson, 1966).

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Molecular Packing Modes of Acyl Halides. I. Introduction

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This is one of seven papers dealing with the effects of the carbonyl halide functional group on the molecular structures and packing modes of five diacyl halides: terephthaloyl chloride, muconyl chloride, biphenyl-2,2′-dicarbonyl chloride, adamantane-1,3-dicarbonyl chloride and terephthaloyl bromide. Interest in the packing modes and molecular geometry originated from work on solid-state chemistry and the need to understand and control the factors determining the structures of molecular crystals. In the absence of a general method for *ab initio* prediction of packing arrangements and conformations in molecular crystals, interest centres on systems containing functional groups, *e.g.* carboxylic acids and amides, whose interactions are relatively stronger than the usual van der Waals forces and often dominate the molecular packing in a predictable way. A survey of available structural data indicated that $X\cdots O$ (X = Cl, Br) interactions exist in some acyl halides and molecular complexes and presumably play, to some extent, a similar role to that of the hydrogen bond in determining the packing arrangements. The aim of the present work was to establish whether the packing modes of diacyl halides are dominated chiefly by the $X\cdots O$ interactions, or whether other factors such as $C^+{=}O^-$ dipole–dipole, $X\cdots X$ or $C{-}H\cdots O$ interactions play a contributive, or even decisive, role in the crystallization of these compounds. A complementary purpose was to augment the available geometrical data on the $-C\overset{O}{\diagdown\!\!\diagup}_{X}$ group.

This series is concerned with the crystallographic studies of the carbonyl halide functional group and its effects on the molecular structures and packing modes of diacyl halides.

In parts II–VI the crystal and molecular structures of five compounds are analysed: terephthaloyl chloride, muconyl chloride, biphenyl-2,2′-dicarbonyl chloride, adamantane-1,3-dicarbonyl chloride and terephthaloyl