

Table 5. Deviations ( $\text{\AA}$ ) of atoms from the best plane through the acridine system

Cl	-0.234	C(7)	-0.054	C(13)	-0.155	C(19)	0.113
O(2)	-0.146	C(8)	-0.092	C(14)	-0.048	C(20)	-0.206
O(3)	0.573	C(9)	-0.052	C(15)	0.183	C(21)	1.141
N(4)	0.066	C(10)	-0.026	C(16)	0.021	C(22)	2.019
N(5)	0.360	C(11)	0.049	C(17)	0.007	C(23)	2.053
N(6)	1.232	C(12)	-0.099	C(18)	0.087	C(24)	1.210

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## The Molecular Structure of $3\beta$ -Acetoxy-20-Hydroxylupane, $C_{32}H_{54}O_3$ .\*

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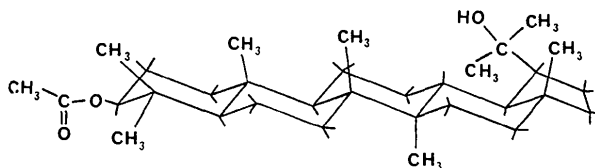
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The structure of the monoacetate derivative of lupane- $3\beta,20$ -diol,  $C_{32}H_{54}O_3$ , was determined by the symbolic-addition procedure and-tangent formula method. The space group is  $P2_1$  and cell dimensions are  $a=15.198$  (8),  $b=8.260$  (7),  $c=12.226$  (5)  $\text{\AA}$  and  $\beta=108.6$  (3) $^\circ$ . The triterpene lupane- $3\beta,20$ -diol,  $C_{30}H_{52}O_2$ , was extracted from *Theolocactus bicolor*, and a monoacetate derivative was prepared. The relative molecular configuration was found to be



The molecule is composed of four *trans* fused six-membered rings and one *trans* fused five-membered ring. All six-membered rings are in the chair conformation. The absolute configuration of the 3-position is known, and the absolute configuration of the remainder of the molecule can be established.

### Introduction

Cacti from the southwestern region of North America are known to contain alkaloids, terpenes, and a variety of other compounds. Frequently, the materials are isolated in small quantities and conventional means of identification are difficult. A small quantity of a white material was isolated from *Theolocactus bicolor*, and preliminary studies indicated the presence of two hydroxyl groups. An acetate derivative was prepared (m.p. 254–256 $^\circ\text{C}$ ), and a mass spectrum was obtained. The derivative was assumed to be a diacetate and the formula  $C_{29}H_{46-48}O_2$  was proposed for the parent com-

pound. This is an unusual formula for a triterpene, although a few compounds of this type have been reported.

Several crystals of the acetate derivative were supplied to our laboratory by Dr Xorge Dominguez who isolated the compound and made the preliminary studies. The crystals of the acetate derivative occur as colorless elongated parallelepipeds. The proposed formula proved to be in error, and the correct formula and structure were established by single-crystal X-ray diffraction techniques.

### Experimental

A crystal of dimensions 1.25 $\times$ 0.35 $\times$ 0.15 mm was mounted with the *b* axis (long dimension) coincident

\* Contribution No. 1 from FASTBIOS Laboratory, Texas Christian University.

with the rotation axis. The unit cell was found to be monoclinic, and cell dimensions were determined from  $b$  axis rotation photographs and  $h0l$  Weissenberg photographs. Sodium chloride lines,  $a = 5.6402 \text{ \AA}$ , were superimposed on the photographs, and the errors are standard deviations obtained from a calculation of the cell edges for a number of reflections. Crystal data are:

$\text{C}_{32}\text{H}_{54}\text{O}_3$ ,  $M = 486$   
 $a = 15.198 \pm 0.008 \text{ \AA}$   $b = 8.260 \pm 0.007 \text{ \AA}$   
 $c = 12.226 \pm 0.005 \text{ \AA}$   $\beta = 108.6 \pm 0.3^\circ$   
 Systematic absences:  $0k0$ ,  $k = 2n + 1$   
 Space group:  $P2_1$ , (No. 4)  
 $Z = 2$ ;  $F(000) = 540$ ;  $V = 1420.2 \text{ \AA}^3$ ;  
 $\mu = 5.49 \text{ cm}^{-1}$  (Cu  $K\alpha$ )  
 $D_{\text{exp}}$  (flotation)  $= 1.12 \text{ g.cm}^{-3}$ ;  
 $D_{\text{calc}} = 1.14 \text{ g.cm}^{-3}$   
 Cu  $K\alpha = 1.54178 \text{ \AA}$ ; graphite monochromator.

Since only five crystals were available, the density was not measured until the structure analysis was completed. The proposed molecular formula for the acetate derivative,  $\text{C}_{33}\text{H}_{52}\text{O}_4$ , gave a calculated density of  $1.20 \text{ g.cm}^{-3}$ . The measured density is more consistent with the molecular formula established by the X-ray analysis.

Data were collected on a Philips PAILRED diffractometer for layers  $h0l$  to  $h6l$  using a scan rate of  $1^\circ/\text{min}$  over a range of  $3.4^\circ$ . A background count of 20 sec was used for the  $h0l$  layer and of 24 sec was used for all others. The intensity of a reference reflection

was monitored to check for crystal deterioration or instrument drift. Of the 2244 independent reflections measured, 1968 were taken to have an observable intensity ( $\sigma_F < \frac{1}{2}F_o$ ). The data were processed on an IBM 1800 computer and were corrected for Lorentz and polarization factors. No absorption corrections were made. The data were adjusted to an absolute scale by a Wilson plot. Standard deviations in observed structure amplitudes,  $\sigma(F_o)$ , were assigned according to:

$$\sigma(F_o) = \frac{1}{2\sqrt{Lp}} \sqrt{\overline{N_s} + R(\overline{Nb_1} + \overline{Nb_2}) + (0.03I_o)^2}.$$

In addition to the structure-factor magnitudes,  $|F_o|$ , the normalized structure-factor magnitudes,  $|E_h|$ , were computed.

### Structure determination and refinement

The structure was solved by the application of the symbolic-addition technique, tangent refinement (Karle & Hauptman, 1956), successive electron-density calculations, and least-squares refinement. Program PHASE, used in the first part of the analysis, was written for the CDC 6600 by Koenig (1969) and was modified for the IBM 1800 by Stemple (1970).

In the early stages of analysis one acetate group was identified, but a second could not be located; however, a fragment resembling a tertiary butyl group always appeared. A tertiary butyl side chain is unusual in a natural product, and it is logical to assume that one

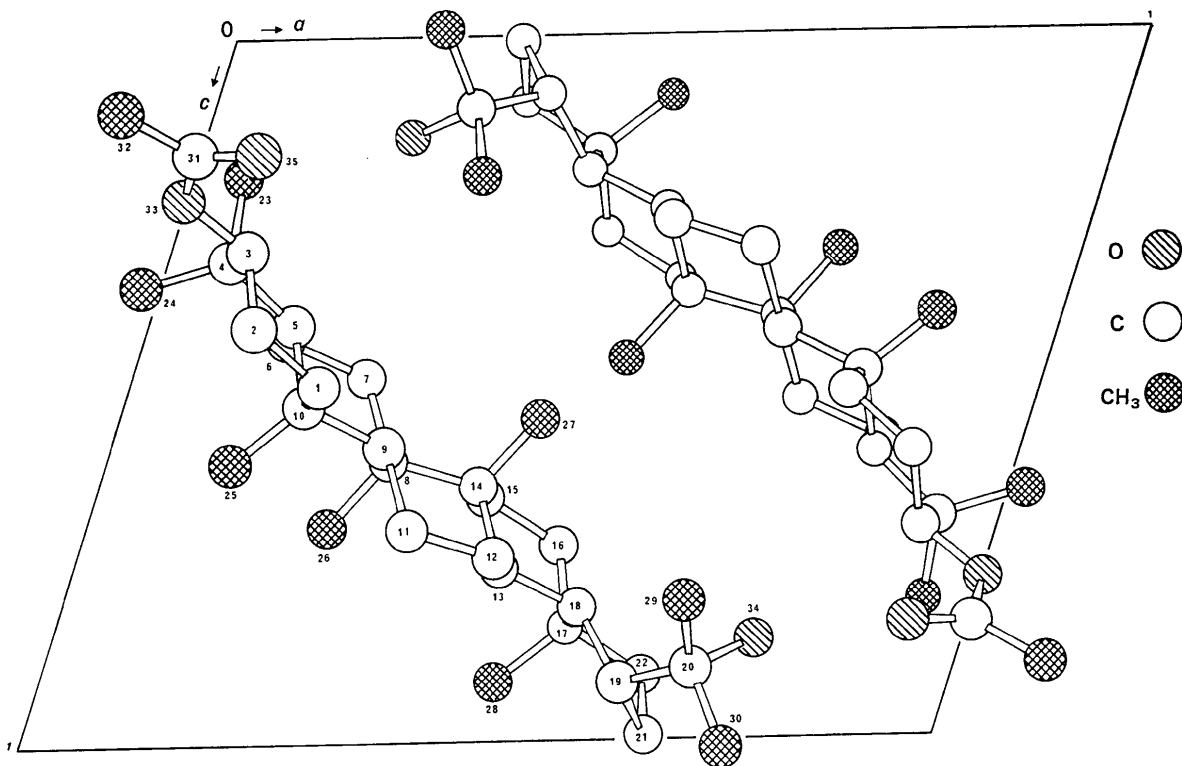


Fig. 1. Contents of unit cell projected down the  $b$  axis.



of the atoms in this group might be a hydroxyl oxygen atom. The tertiary hydroxyl would be difficult to acetylate, and a monoacetate derivative would be formed.

With this assumption, the analysis was continued and a formula of  $C_{32}H_{54}O_3$  was established.

At this point one of the crystals was used to obtain a

Table 2. Fractional coordinates ( $\times 10^4$ ) and anisotropic temperature factors for  $3\beta$ -acetoxy-20-hydroxylupane†

Thermal parameters are of the form:

$$\exp [-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*})].$$

	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	2083 (7)	10461 (5)	4923 (10)	3.4 (5)	4.5 (7)	5.6 (6)	2.4 (9)	-2.7 (9)	-2.2 (10)
C(2)	1177 (8)	11206 (6)	4080 (11)	4.8 (6)	3.6 (6)	5.8 (7)	2.3 (10)	-1.4 (10)	0.9 (10)
C(3)	0841 (7)	10319 (5)	2993 (9)	2.1 (4)	4.3 (6)	3.9 (5)	1.7 (8)	1.0 (8)	2.0 (9)
C(4)	0685 (7)	8486 (5)	3133 (9)	2.4 (4)	4.6 (7)	3.9 (5)	-0.3 (9)	1.2 (8)	-0.7 (9)
C(5)	1604 (7)	7840 (5)	4054 (9)	2.5 (4)	3.4 (6)	3.1 (5)	0.8 (8)	1.4 (8)	-0.6 (9)
C(6)	1565 (8)	5989 (6)	4257 (11)	4.1 (6)	4.7 (8)	4.3 (6)	-1.9 (10)	-2.2 (9)	0.0 (11)
C(7)	2580 (8)	5333 (6)	4808 (10)	4.4 (5)	2.0 (6)	5.4 (6)	-0.3 (9)	0.1 (9)	-1.1 (10)
C(8)	3103 (7)	6184 (5)	5978 (9)	3.5 (5)	2.3 (5)	3.2 (5)	-0.1 (8)	0.7 (8)	-0.0 (9)
C(9)	3015 (6)	7969 (4)	5801 (7)	2.7 (4)	3.0 (5)	2.5 (4)	-0.3 (7)	1.1 (7)	0.3 (7)
C(10)	1993 (6)	8713 (5)	5205 (9)	3.1 (5)	2.9 (6)	3.8 (5)	1.7 (8)	0.4 (8)	1.3 (9)
C(11)	3542 (8)	8862 (5)	6969 (9)	4.9 (6)	4.2 (6)	4.3 (5)	3.1 (10)	1.3 (9)	0.9 (10)
C(12)	4587 (7)	8344 (5)	7378 (9)	3.9 (5)	4.4 (6)	3.4 (5)	1.0 (9)	-2.0 (8)	-1.0 (9)
C(13)	4675 (6)	6539 (5)	7522 (8)	3.0 (4)	3.4 (6)	3.2 (5)	1.7 (8)	1.9 (8)	1.2 (8)
C(14)	4178 (6)	5654 (5)	6366 (8)	2.6 (4)	2.4 (6)	3.7 (5)	1.2 (7)	0.7 (7)	0.5 (8)
C(15)	4293 (8)	3727 (6)	6518 (10)	3.8 (5)	4.6 (7)	5.5 (6)	-0.6 (10)	0.5 (9)	-1.5 (11)
C(16)	5266 (8)	3097 (6)	7217 (11)	4.5 (6)	2.5 (6)	7.7 (7)	2.1 (10)	2.4 (10)	-0.2 (11)
C(17)	5631 (8)	4013 (6)	8365 (10)	3.2 (5)	5.7 (7)	4.9 (6)	1.2 (9)	-0.2 (9)	1.7 (11)
C(18)	5674 (7)	5857 (5)	8096 (8)	3.5 (4)	2.8 (6)	2.7 (4)	0.5 (8)	1.4 (7)	-0.7 (8)
C(19)	6385 (7)	6694 (5)	9183 (9)	3.6 (4)	4.4 (6)	3.5 (5)	2.1 (8)	0.5 (8)	-0.7 (9)
C(20)	7128 (8)	7859 (6)	8986 (11)	3.6 (5)	7.00 (7)	6.1 (7)	0.8 (10)	1.4 (10)	-1.5 (13)
C(21)	6842 (9)	5073 (7)	9929 (12)	5.0 (7)	10.4 (10)	6.1 (8)	5.4 (14)	-3.1 (11)	-0.6 (16)
C(22)	6610 (9)	3686 (6)	9076 (11)	6.0 (7)	3.4 (7)	7.4 (8)	2.4 (11)	-0.9 (11)	1.9 (11)
C(23)	0551 (9)	7626 (6)	1933 (10)	4.9 (6)	7.6 (9)	3.8 (6)	2.8 (12)	-0.8 (10)	-2.7 (12)
C(24)	-0200 (7)	8256 (6)	3480 (11)	2.1 (4)	7.2 (8)	6.7 (7)	-1.8 (10)	1.2 (9)	4.5 (13)
C(25)	1380 (8)	8730 (5)	6010 (9)	4.2 (5)	7.5 (7)	3.1 (5)	3.0 (11)	3.6 (9)	0.6 (12)
C(26)	2656 (8)	5610 (6)	6923 (11)	3.2 (5)	6.6 (8)	5.9 (7)	1.4 (10)	5.0 (10)	5.2 (12)
C(27)	4630 (7)	6103 (5)	5422 (9)	3.9 (5)	6.5 (6)	2.7 (5)	0.5 (10)	2.5 (8)	2.1 (10)
C(28)	5013 (10)	3677 (7)	9143 (12)	6.9 (7)	7.9 (8)	7.0 (8)	0.7 (14)	6.0 (13)	6.9 (15)
C(29)	6831 (10)	8992 (7)	8034 (14)	7.4 (8)	6.6 (8)	9.0 (9)	-2.8 (13)	1.7 (15)	1.6 (16)
C(30)	7739 (10)	8536 (7)	10120 (13)	7.3 (8)	9.1 (10)	8.2 (8)	-1.6 (15)	-0.9 (8)	-9.7 (16)
C(31)	-0054 (8)	12237 (6)	1619 (12)	3.3 (6)	7.1 (9)	5.1 (7)	0.2 (11)	2.7 (10)	3.3 (13)
C(32)	-1015 (8)	12922 (6)	1011 (12)	3.8 (6)	8.8 (9)	6.0 (7)	6.7 (12)	1.2 (10)	5.4 (14)
O(33)	-0031 (5)	10990 (4)	2254 (7)	3.2 (4)	5.6 (5)	4.6 (4)	0.9 (6)	1.3 (6)	2.8(8)
O(34)	7728 (6)	6700 (5)	8592 (10)	4.6 (4)	11.6 (7)	13.4 (8)	-0.3 (10)	8.1 (10)	5.8 (13)
O(35)	0636 (6)	12984 (5)	1628 (9)	5.8 (5)	12.8 (7)	9.8 (6)	5.2 (10)	5.9 (9)	11.0 (12)
H(1)	2585	10583	4600	‡					
H(1')	2278	11089	5631						
H(2)	1287	12327	3926						
H(2')	0698	11223	4448						
H(3)	1302	10370	2598						
H(5)	1997	0805	3582						
H(6)	1274	5450	3525						
H(6')	1210	5784	4777						
H(7)	2925	5486	4271						
H(7')	2562	4175	4930						
H(9)	3283	8285	5212						
H(11)	3497	10024	6847						
H(11')	3263	8570	7552						
H(12)	4808	8692	6815						
H(12')	317	8867	8107						
H(13)	4317	6407	8046						
H(15)	4092	3213	5765						
H(15')	3838	3311	6851						
H(16)	5688	3254	6775						
H(16')	5231	1950	7367						
H(18)	6036	6008	7579						
H(19)	6017	7270	9575						
H(21)	7510	5198	10237						
H(21')	6556	4887	10523						
H(22)	7005	3737	8592						
H(22')	6641	2673	9489						

† Standard deviations of last significant figures are given in parentheses.

‡ Isotropic temperature factor of 2.0 used for all hydrogen atoms.

mass spectrum. The highest observed mass peak occurred at 468 which is less than the molecular weight of the proposed structure; however, tertiary alcohols seldom exhibit a parent ion peak in the mass spectrum (Beynon, 1960). The true parent ion eliminates water, and the observed mass is 18 units too small. The addition of 18 mass units yields a molecular weight of 486, corresponding to that of the structure proposed by X-ray analysis. The molecular formula of the isolated natural product is C<sub>30</sub>H<sub>52</sub>O<sub>2</sub>. Density by the flotation technique, using a sodium chloride solution, was determined from one crystal. The observed value of 1.12

g.cm<sup>-3</sup> corresponds well with the calculated value of 1.14 g.cm<sup>-3</sup>.

Positional and anisotropic thermal parameters were refined on an IBM 1800 computer using a block-diagonal least-squares approximation. The program minimized the function  $\sum w(|F_o| - |kF_c|)^2$  where  $w = 1/[\sigma(F_o)]^2$ . Scattering factors of Cromer & Waber (1965) were used for the carbon and oxygen atoms; hydrogen scattering factors were those calculated by Stewart, Davidson & Simpson (1965). Atomic positions of the ring hydrogen atoms were calculated by assuming a tetrahedral angle and a C-H distance of 0.97 Å. The

Table 3. *Interatomic distances and bond angles for 3 $\beta$ -acetoxy-20-hydroxylupane*

C(1)—C(2)	1.559 (13) Å	C(13)—C(14)	1.557 (12) Å
C(1)—C(10)	1.501 (7)	C(13)—C(18)	1.560 (10)
C(2)—C(3)	1.460 (14)	C(14)—C(15)	1.606 (6)
C(3)—C(4)	1.551 (6)	C(14)—C(27)	1.564 (12)
C(3)—O(33)	1.455 (10)	C(15)—C(16)	1.543 (13)
C(4)—C(5)	1.582 (12)	C(16)—C(17)	1.534 (16)
C(4)—C(23)	1.583 (15)	C(17)—C(18)	1.563 (7)
C(4)—C(24)	1.545 (10)	C(17)—C(22)	1.489 (14)
C(5)—C(6)	1.553 (7)	C(17)—C(28)	1.561 (15)
C(5)—C(10)	1.523 (13)	C(18)—C(19)	1.581 (12)
C(6)—C(7)	1.571 (12)	C(19)—C(20)	1.559 (9)
C(7)—C(8)	1.564 (14)	C(19)—C(21)	1.643 (11)
C(8)—C(9)	1.490 (6)	C(20)—C(29)	1.449 (16)
C(8)—C(14)	1.609 (10)	C(20)—C(30)	1.509 (18)
C(8)—C(26)	1.588 (13)	C(20)—O(34)	1.504 (9)
C(9)—C(10)	1.613 (9)	C(21)—C(22)	1.513 (14)
C(9)—C(11)	1.579 (12)	C(31)—C(32)	1.521 (13)
C(10)—C(25)	1.556 (12)	C(31)—O(33)	1.284 (10)
C(11)—C(12)	1.565 (11)	C(31)—O(35)	1.213 (9)
C(12)—C(13)	1.503 (6)	O(34)—O(35')	2.793 (7)
C(2)—C(1)—C(10)	113.9 (6)°	C(1)—C(10)—C(9)	109.0 (5)°
C(1)—C(2)—C(3)	112.5 (6)	C(1)—C(10)—C(5)	106.3 (8)
C(2)—C(3)—C(4)	114.2 (8)	C(1)—C(10)—C(25)	104.6 (5)
C(2)—C(3)—O(33)	111.0 (5)	C(5)—C(10)—C(9)	105.8 (5)
C(4)—C(3)—O(33)	107.4 (5)	C(5)—C(10)—C(25)	117.0 (6)
C(3)—C(4)—C(5)	106.0 (6)	C(9)—C(10)—C(25)	113.7 (7)
C(3)—C(4)—C(23)	108.3 (7)	C(9)—C(11)—C(12)	109.4 (6)
C(3)—C(4)—C(24)	109.2 (4)	C(11)—C(12)—C(13)	110.6 (5)
C(5)—C(4)—C(23)	109.4 (6)	C(12)—C(13)—C(14)	111.1 (7)
C(5)—C(4)—C(24)	114.3 (8)	C(12)—C(13)—C(18)	116.7 (5)
C(23)—C(4)—C(24)	109.5 (7)	C(14)—C(13)—C(18)	111.1 (5)
C(4)—C(5)—C(6)	112.1 (6)	C(8)—C(14)—C(13)	107.1 (5)
C(4)—C(5)—C(10)	119.5 (5)	C(8)—C(14)—C(15)	111.5 (5)
C(6)—C(5)—C(10)	110.0 (8)	C(8)—C(14)—C(27)	111.2 (7)
C(5)—C(6)—C(7)	109.0 (6)	C(13)—C(14)—C(15)	110.9 (7)
C(6)—C(7)—C(8)	112.4 (6)	C(13)—C(14)—C(27)	111.0 (5)
C(7)—C(8)—C(9)	108.4 (7)	C(15)—C(14)—C(27)	105.3 (5)
C(7)—C(8)—C(14)	108.6 (6)	C(14)—C(15)—C(16)	116.6 (6)
C(7)—C(8)—C(26)	108.7 (6)	C(15)—C(16)—C(17)	110.1 (6)
C(9)—C(8)—C(14)	110.4 (5)	C(16)—C(17)—C(18)	108.3 (8)
C(9)—C(8)—C(26)	111.2 (6)	C(16)—C(17)—C(22)	116.6 (7)
C(14)—C(8)—C(26)	109.5 (7)	C(16)—C(17)—C(28)	111.0 (7)
C(8)—C(9)—C(10)	118.2 (5)	C(18)—C(17)—C(22)	101.5 (5)
C(8)—C(9)—C(11)	109.6 (7)	C(18)—C(17)—C(28)	112.0 (6)
C(10)—C(9)—C(11)	111.6 (5)	C(22)—C(17)—C(28)	107.2 (10)
C(13)—C(18)—C(17)	110.3 (5)	C(29)—C(20)—C(30)	116.2 (7)
C(13)—C(18)—C(19)	121.8 (5)	C(29)—C(20)—O(34)	102.6 (9)
C(17)—C(18)—C(19)	108.2 (7)	C(30)—C(20)—O(34)	105.8 (7)
C(18)—C(19)—C(20)	118.4 (8)	C(19)—C(21)—C(22)	105.7 (9)
C(18)—C(19)—C(21)	99.5 (5)	C(17)—C(22)—C(21)	103.6 (6)
C(20)—C(19)—C(21)	113.0 (6)	C(32)—C(31)—O(33)	115.5 (7)
C(19)—C(20)—C(29)	117.9 (8)	C(32)—C(31)—O(35)	120.5 (7)
C(19)—C(20)—C(30)	110.5 (9)	O(33)—C(31)—O(35)	123.1 (9)
C(19)—C(20)—O(34)	101.5 (4)	C(3)—O(33)—C(31)	121.7 (6)

contributions from these hydrogen atoms were calculated, but the positions were not refined. After each cycle of refinement, hydrogen positions were recalculated. The refinement was terminated when the conventional  $R$  value reached 0.090 with 1358 reflections included in the refinement. The  $R$  value for all 1968 observed reflections is 0.109. Standard deviations were estimated from the inverse of the normal equations matrices in the last block-diagonal least-squares refinement. The exact relationship between these standard deviations and those calculated from a full-matrix refinement is not known; however, a comparison with standard deviations calculated from one cycle of full-matrix refinement indicated the proportionality constant to be approximately 1.0. Usually, the ratio is larger, as indicated by test studies on other compounds. This uncertainty in standard deviations should be considered if any detailed comparisons are made with other compounds.

A final difference Fourier synthesis indicated no peak as large as  $0.5 \text{ e.}\text{\AA}^{-3}$ . Squares of observed and calculated structure factors are listed in Table 1. Positional and thermal parameters are given in Table 2. Bond lengths and bond angles are listed in Table 3. Fig. 1 is a projection of unit-cell contents down the  $b$  axis. Fig. 2 shows the accepted numbering system for the triterpene portion of the molecule. Additional atoms have been numbered consecutively.

#### Discussion

The investigated molecule proved to be the monoacetate derivative of lupane- $3\beta,20$ -diol, a triterpene which has been found in the roots and fruit of the Osage orange, *Maclura pomifera* (Douglas & Lewis, 1966; Lewis, 1959) and in the bark of the birch, *Betula ver-*

*rucosa* Erh. (Lindgren & Svahn, 1966). Lewis (1959) reported that only the monoacetate derivative of lupane- $3\beta,20$ -diol could be prepared by acetylation, and the melting point of the monoacetate was reported as  $248\text{--}250^\circ\text{C}$ . These data are consistent with the structure and properties of the compound we report. The stereochemistry and reactions of several related compounds have been reported (Barton & Holness, 1952; Halsall, Jones & Meakins, 1952; Ames, Halsall & Jones, 1951).

The structure contains four six-membered rings and one five-membered ring which are all *trans* fused. All six-membered rings are in the chair conformation. Average C-C distance within the rings is  $1.56(4) \text{ \AA}$ , with no indication of any double bond. The average bond angle within the six-membered rings is  $111(4)^\circ$ . Average bond angle within the five-membered ring is  $104(3)^\circ$ . The acetate group is identified readily, but the hydroxyl group might be atom 29, or 30, or 34. The carbonyl oxygen atom (35) of an adjacent molecule lies within  $2.793(7) \text{ \AA}$  of the atom labeled (34). It is logical to assume that hydrogen bonding occurs between two molecules, and atom (34) was designated as the oxygen atom during refinement; however, the three distances  $\text{C}(20)\text{--}\text{O}(34) = 1.504(9)$ ,  $\text{C}(20)\text{--}\text{C}(29) = 1.449(16)$ , and  $\text{C}(20)\text{--}\text{C}(30) = 1.509(18) \text{ \AA}$  introduces some uncertainty into this assignment. Some disordering may be associated with these positions. The specific assignment of the oxygen atom is not important in identifying the natural product.

The absolute configuration of the molecule was not determined in this study; however, there is chemical evidence that the absolute configuration at the three-position is the configuration designated as  $\beta$  (Simonsen & Ross, 1957). If this assignment is correct, the stereo-

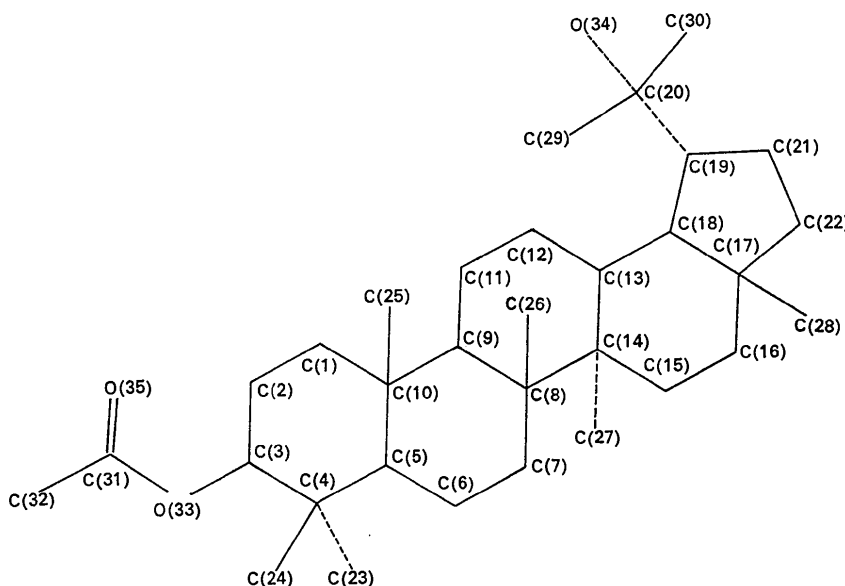


Fig. 2. Numbering system and stereochemical representation of  $3\beta$ -acetoxy-20-hydroxylupane.

chemistry of the entire molecule is determined. This absolute configuration is presented in Figs. 1 & 2.

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## The Crystal Structure of Rubidium 7,7,8,8-Tetracyanoquinodimethane, Rb-TCNQ, at $-160^{\circ}\text{C}$

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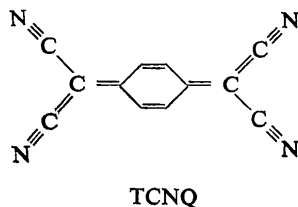
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Crystals of Rb-TCNQ have monoclinic symmetry; the space group is  $P2_1/c$ ,  $a = 7.187$  (1),  $b = 12.347$  (2),  $c = 13.081$  (3) Å,  $\beta = 98.88$  (2)°,  $Z = 4$ . Rb<sup>+</sup> and TCNQ<sup>-</sup> are both at general positions. The intensities were collected at  $-160^{\circ}\text{C}$  on an automatic Nonius diffractometer. Approximate values for the atomic coordinates were obtained from Patterson and difference Fourier maps. Anisotropic least-squares refinement decreased the residual  $R$  to 0.066 for 5512 independent reflexions. The bond lengths in the TCNQ<sup>-</sup> ion show that the ion has quinoid character; the group is not planar but has the shape of a shallow boat. The TCNQ<sup>-</sup> radical-ions form charge-resonance bounded rows along the  $a$  axis. The interaction between the rows is small. Within a row interplanar spacings of 3.159 and 3.484 Å alternate. The distance of 3.159 Å is the shortest distance found so far between successive TCNQ planes. The Rb<sup>+</sup> ions also form rows along the  $a$  axis with alternating distances of 3.483 and 3.726 Å between the ions. These distances are appreciably longer than twice the radius of Rb<sup>+</sup> (3.0 Å). Rb<sup>+</sup> is octahedrally surrounded by eight negatively charged TCNQ nitrogen atoms at distances of 2.982, 2.996, 3.004, 3.009, 3.025, 3.055, 3.057 and 3.108 Å.

#### Introduction

Salts of the stable TCNQ<sup>-</sup> radical anion, derived from 7,7,8,8-tetracyanoquinodimethane (TCNQ), show interesting electrical and magnetic properties.



Some of these organic radical salts are among the

organic compounds with the highest electrical conductivities known, approximately  $100 \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature, whereas for others the conductivity is as small as  $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature (Acker, Harder, Hertler, Mahler, Melby, Benson & Mochel, 1960; Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962). Recent measurements of the electrical conductivities and absolute magnetic susceptibilities of the crystalline M<sup>1</sup>-TCNQ salts (M<sup>1</sup> = alkali cation) have revealed that phase transitions occur in all these salts except in Li-TCNQ (Vegter, Hibma & Kommandeur, 1969). Table 1 shows that especially for Rb-TCNQ the heat of transition is large. We observed that crystals of this compound do not remain single during the transition, indicating that the changes in the structure are pronounced.