

## Crystal and Molecular Structure and Absolute Configuration of 3 $\beta$ -Acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetraene, a Stable Dithiete Compound

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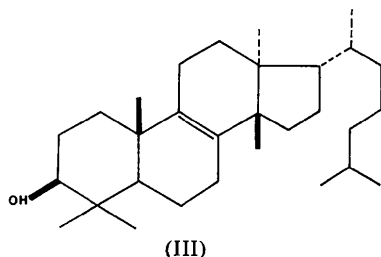
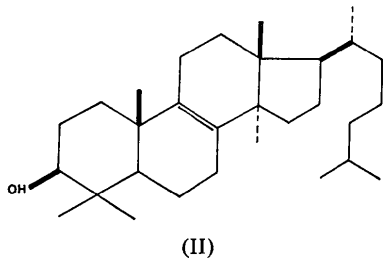
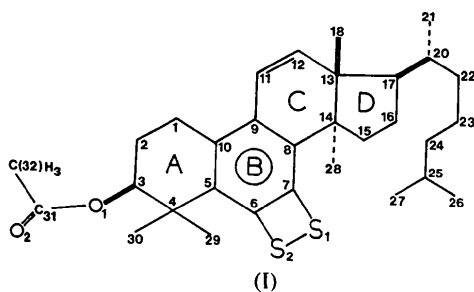
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The structure and absolute configuration of 3 $\beta$ -acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetraene have been determined by X-ray methods. The crystals are monoclinic,  $P2_1$ ,  $a=20.1896$ ,  $b=11.0709$ ,  $c=6.4953$  Å,  $\beta=90.578^\circ$ ,  $Z=2$ . The structure was solved by Fourier methods, and refined by full-matrix least squares to  $R=3.4\%$  on 2362 'observed' reflexions. The S-S length in the dithiete ring is 2.12 Å, and the two S-C-C angles are 100 and 103°. There are no abnormal intermolecular contacts, the shortest S...S distance being about 10 Å. The compound is the first reported representative of its class.

### Introduction

3 $\beta$ -Acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetraene (I) is a stable dithiete tautomer of a dithio-*o*-quinone. It was obtained during an attempt to convert a derivative of lanostenol (II) into a derivative of euphenol (III) through the series of reactions (IV) to (VII). There are very few authenticated reports of 1,2-dithiones (VIII) or their valence tautomers, 1,2-dithietes (IX) (Kusters & de Mayo, 1974). The present compound is believed to be the first representative of its class.



A preliminary report of the preparation and structure of (I) has been published (Boar, Hawkins, McGhie, Misra, Barton, Ladd & Povey, 1975), and a full account of the chemistry of the compound will be published (Boar, 1975). This paper describes the crystallography of the title compound.

### Experimental

The compound (I) was recrystallized from 1:1 dichloromethane-methanol as pale-yellow, lath-like parallelepipeda elongated along  $z$ . The crystal forms present were {100}, {010} and {001}, in decreasing order of development. An optical examination suggested that the crystals were monoclinic. Oscillation and Weissenberg photographs confirmed this, provided approximate cell dimensions, and showed that the only systematic extinctions were  $0k0$  for  $k=2n+1$ ; hence, the space group is either  $P2_1$  or  $P2_1/m$ .

The density was measured by flotation in aqueous sodium bromide at 25°C. The result, 1.17 g cm<sup>-3</sup>, was obtained by measuring the refractive index of the flotation-equilibrium solution and then obtaining the density from a calibration chart. Since, from the cell volume,  $Z=2$ , the space group  $P2_1/m$  was eliminated for crystals of the asymmetric molecule under investigation.

Accurate cell dimensions were obtained from a least-squares fit to the  $\theta$ -values of 30 reflexions with  $\theta > 49^\circ$ , measured on a Siemens four-circle diffractometer (A.E.D.). Resolution of the Cu  $K\alpha_1$  ( $\lambda=1.54056$  Å) and Cu  $K\alpha_2$  ( $\lambda=1.54439$  Å) peaks was obtained for these reflexions, which were chosen so as to be evenly distributed in reciprocal space. The crystal data are listed in Table 1.

The intensities of 2605 symmetry-independent reflexions with  $(\sin \theta)\lambda \leq 0.60$  were measured on the diffractometer by a five-value measurement technique (Hoppe, 1965). Of these reflexions, 243 for which  $I < 2.580\sigma(I)$  were classed as unobserved. The average standard deviations of the  $|F_o|$  data were 1.8%

Table 1. *Crystal data*

3 $\beta$ -Acetoxy-6,7-epidithio- -19-norlanosta-5,7,9,11-tetraene	C <sub>31</sub> H <sub>44</sub> O <sub>2</sub> S <sub>2</sub>	<i>a</i>	20.1896 (9) Å
F. W.	512.82	<i>b</i>	11.0709 (5)
m. p.	161–163°C	<i>c</i>	6.4953 (3)
System	Monoclinic	$\beta$	90.578 (2)°
Space group	<i>P</i> 2 <sub>1</sub>	<i>V</i> <sub>c</sub>	1451.6 (1) Å <sup>3</sup>
Crystal dimensions	0.2 × 0.3 × 0.5 mm    <i>a</i> , <i>b</i> , <i>c</i>	<i>D</i> <sub>m</sub>	1.17 (1) g cm <sup>-3</sup>
$\sum Z^2(S)/\sum Z^2(\text{light atoms})$	0.4	<i>D</i> <sub>c</sub>	1.173 (1)
<i>F</i> (000)	556	<i>Z</i>	2
$\mu(\text{Cu } K\alpha)$	19 cm <sup>-1</sup>		

(observed) and 2.7% (all reflexions). The unobserved reflexions were omitted from the structure analysis.

A reference reflexion (740,  $|F_o|=46$ ) was measured after every 20 reflexions. The data were scaled, first within the batches of 20 reflexions and then to the average value of the reference reflexion. The scaling factors varied over a range of less than  $\pm 2\%$ , and there was no evidence of crystal decomposition.

Corrections were applied for Lorentz and polarization effects, but not for absorption ( $\mu R=0.78$ ).  $|E|$  values were calculated by the *K*-curve method. The statistics are listed in Table 2; they show good agreement with those for the idealized acentric distribution.

Table 2. *Statistics of |E| values*

	This structure	Acentric	Centric
$\overline{ E ^2}$	1.00	1.00	1.00
$\overline{ E }$	0.88	0.89	0.80
$\overline{ E ^2-1}$	0.76	0.74	0.97
% $\geq 1.5$	11.2	10.5	13.4
% $\geq 1.75$	4.7	4.7	8.0
% $\geq 2.0$	2.4	1.8	4.6
% $\geq 2.5$	0.4	0.2	1.2

#### Structure determination and refinement

Patterson and sharpened ( $|E|^2-1$ ) Patterson syntheses showed four large peaks of heights which were

Table 3. *Fractional coordinates ( $\times 10^4$ , except H  $\times 10^3$ ) and temperature factors ( $\times 10^3$ ), with e.s.d.'s in parentheses*

Anisotropic temperature factors were of the form  $\exp\{-2\pi\lambda^{-2}[h^2a^{*2}U_{11} + \dots + hka^*b^*U_{12} + \dots]\}$ , and isotropic temperature factors were of the form  $\exp[-8\pi^2U_{iso}(\sin^2\theta)/\lambda^2]$ . In the notation for H atoms, the first digit, or the first two where there are three, denotes the number of the C atom to which H is bonded. (\* indicates calculated coordinates, assuming C-H = 1.00 Å and H-C-C = 109° 44'.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>31</sub>	<i>U</i> <sub>23</sub>
S(1)	2092 (1)	7500 (0)	-1522 (2)	47 (1)	69 (1)	58 (1)	-2 (0)	1 (0)	20 (0)
S(2)	1095 (1)	6933 (1)	-1216 (2)	42 (1)	67 (1)	58 (1)	3 (0)	5 (0)	11 (0)
O(1)	-216 (1)	3997 (3)	4916 (5)	38 (1)	60 (2)	62 (2)	-9 (1)	11 (1)	-9 (1)
O(2)	-556 (2)	5481 (3)	7003 (6)	56 (2)	87 (2)	92 (3)	-1 (2)	16 (2)	-31 (2)
C(1)	1629 (2)	4153 (4)	5549 (7)	40 (2)	55 (2)	53 (2)	-3 (2)	3 (2)	10 (2)
C(2)	948 (2)	3566 (4)	5356 (7)	43 (2)	55 (2)	56 (2)	-4 (2)	11 (2)	5 (2)
C(3)	447 (2)	4519 (3)	4784 (6)	32 (2)	53 (2)	51 (2)	-8 (1)	5 (2)	-5 (2)
C(4)	553 (2)	5010 (3)	2608 (6)	35 (2)	51 (2)	54 (2)	-2 (1)	0 (2)	0 (2)
C(5)	1275 (2)	5406 (3)	2437 (6)	33 (2)	44 (2)	49 (2)	-1 (1)	3 (1)	0 (1)
C(6)	1482 (2)	6170 (3)	890 (6)	38 (2)	47 (2)	47 (2)	2 (1)	-2 (2)	0 (2)
C(7)	2131 (2)	6556 (3)	670 (6)	35 (2)	47 (2)	48 (2)	0 (1)	3 (2)	4 (1)
C(8)	2626 (2)	6239 (3)	2052 (6)	38 (2)	50 (2)	41 (2)	-2 (1)	4 (2)	4 (1)
C(9)	2439 (2)	5457 (3)	3650 (6)	34 (2)	49 (2)	46 (2)	-1 (1)	4 (1)	3 (2)
C(10)	1778 (2)	5023 (3)	3822 (6)	36 (2)	49 (2)	44 (2)	-0 (1)	1 (1)	-1 (1)
C(11)	2956 (2)	5113 (4)	5149 (7)	44 (2)	70 (3)	48 (2)	-6 (2)	-2 (2)	14 (2)
C(12)	3606 (2)	5283 (4)	4789 (7)	35 (2)	73 (3)	54 (2)	-1 (2)	-6 (2)	13 (2)
C(13)	3818 (2)	5765 (3)	2728 (7)	36 (2)	52 (2)	54 (2)	-1 (1)	3 (2)	9 (2)
C(14)	3318 (2)	6772 (3)	2105 (6)	35 (2)	49 (2)	54 (2)	-5 (1)	0 (2)	6 (2)
C(15)	3617 (2)	7248 (4)	95 (7)	40 (2)	68 (2)	65 (2)	-6 (2)	6 (2)	16 (2)
C(16)	4373 (2)	7234 (4)	595 (8)	39 (2)	71 (3)	84 (3)	-7 (2)	5 (2)	17 (2)
C(17)	4489 (2)	6461 (4)	2536 (7)	36 (2)	64 (3)	68 (3)	1 (2)	5 (2)	8 (2)
C(18)	3794 (2)	4713 (4)	1196 (8)	54 (3)	56 (2)	77 (3)	2 (2)	11 (2)	-1 (2)
C(20)	5126 (2)	5710 (5)	2419 (10)	36 (2)	79 (3)	107 (4)	0 (2)	9 (2)	22 (3)
C(21)	-4783 (3)	4859 (7)	4209 (15)	43 (3)	135 (6)	164 (7)	15 (3)	0 (4)	69 (5)
C(22)	-4265 (3)	6539 (5)	2226 (11)	43 (3)	82 (3)	124 (5)	-3 (2)	14 (3)	14 (3)
C(23)	-3667 (3)	5909 (6)	1328 (14)	49 (3)	93 (4)	149 (6)	0 (3)	24 (3)	0 (4)
C(24)	-3063 (3)	6698 (6)	1119 (13)	61 (3)	83 (4)	156 (6)	-8 (3)	28 (4)	-8 (4)
C(25)	-2507 (3)	6192 (5)	-131 (11)	65 (3)	88 (4)	106 (5)	-1 (3)	27 (3)	0 (3)
C(26)	-1882 (6)	6771 (17)	192 (38)	109 (8)	337 (20)	527 (34)	-100 (11)	149 (14)	-293 (23)
C(27)	-2637 (9)	6554 (14)	-2374 (22)	267 (18)	206 (13)	148 (11)	62 (11)	68 (11)	25 (9)
C(28)	3291 (2)	7829 (4)	3650 (7)	46 (2)	58 (2)	72 (3)	-3 (2)	4 (2)	-8 (2)
C(29)	82 (2)	6081 (4)	2263 (8)	33 (2)	69 (3)	84 (3)	5 (2)	6 (2)	14 (2)
C(30)	414 (2)	4042 (4)	959 (7)	57 (3)	73 (3)	53 (2)	-16 (2)	6 (2)	-10 (2)
C(31)	-664 (2)	4563 (4)	6101 (7)	41 (2)	63 (2)	52 (2)	1 (2)	9 (2)	4 (2)
C(32)	-1309 (2)	3881 (5)	6078 (9)	45 (3)	81 (3)	85 (3)	-2 (2)	16 (2)	3 (3)

Table 3 (cont.)

	x	y	z	$U_{iso}$
H(11)	203 (2)	346 (4)	569 (7)	53 (11)
H(12)	166 (0)	465 (0)	674 (0)	65 (13)
H(21)	84 (2)	313 (0)	657 (0)	59 (13)
H(22)	100 (2)	297 (0)	433 (0)	42 (10)
H(31)	50 (2)	521 (3)	568 (0)	39 (10)
H(111)	281 (2)	467 (4)	644 (8)	65 (13)
H(121)	394 (3)	507 (5)	577 (9)	85 (17)
H(151)	348 (2)	812 (4)	-24 (7)	57 (12)
H(152)	355 (3)	667 (4)	-117 (8)	65 (14)
H(161)	452 (3)	804 (4)	87 (8)	72 (14)
H(162)	472 (3)	691 (5)	-84 (9)	87 (16)
H(171)	457 (2)	702 (5)	375 (8)	72 (14)
H(181)	329 (3)	446 (5)	79 (9)	78 (15)
H(182)	398 (4)	502 (6)	3 (12)	115 (23)
H(183)	411 (2)	403 (4)	170 (7)	57 (12)
H(201)	506 (4)	512 (6)	111 (12)	112 (22)
H(211)	521 (3)	537 (6)	561 (11)	97 (19)
H(212)	485 (4)	414 (5)	415 (11)	96 (19)
H(213)	557 (5)	439 (8)	420 (16)	168 (35)
H(221)	-423 (4)	683 (7)	373 (12)	122 (23)
H(222)	568 (3)	721 (6)	134 (11)	106 (21)
H(231)	626 (6)	508 (9)	148 (18)	180 (38)
H(232)	-390 (5)	588 (9)	-58 (18)	164 (34)
H(241)	-309 (3)	748 (5)	141 (9)	88 (18)
H(242)	704 (9)	645 (17)	296 (32)	303 (86)
H(251)	-272 (5)	499 (9)	-28 (18)	188 (39)
H(261)	-192	765	-18	100
H(262)	-175	669	167	100
H(263)	-154	638	-69	100
H(271)	-307	621	-285	100
H(272)	-265	745	-248	100
H(273)	-227	623	-326	100
H(281)	370 (3)	836 (4)	352 (8)	69 (14)
H(282)	292 (3)	840 (5)	317 (9)	76 (15)
H(283)	321 (3)	752 (4)	509 (8)	77 (15)
H(291)	-38 (3)	589 (5)	247 (10)	85 (17)
H(292)	10 (3)	637 (4)	88 (8)	64 (13)
H(293)	18 (3)	671 (5)	335 (10)	99 (19)
H(301)	-949 (3)	429 (4)	-44 (8)	68 (14)
H(302)	69 (2)	331 (4)	121 (7)	49 (11)
H(303)	-8 (3)	378 (4)	112 (9)	74 (15)
H(321)	844 (6)	381 (10)	440 (20)	180 (41)
H(322)	875 (3)	300 (5)	608 (9)	87 (18)
H(323)	850 (4)	394 (7)	725 (13)	110 (24)

equal within 5%. However, the geometry of their positions was in accord with that of two pairs of S atoms, the atoms in each pair being related by  $2_1$  symmetry. The coordinates of both S atoms were deduced. The y coordinate of S(1) was fixed at  $\frac{1}{2}$ , and that of S(2) was deduced to be 0.69. Their difference, 0.66 Å, was

sufficient to break the pseudo-symmetry which occurs in  $P2_1$  where the unit cell contains only two heavy atoms. A similar situation has been reported for epilimonil iodoacetate (Arnott, Davie, Robertson, Sim & Watson, 1961).

Two cycles of successive Fourier syntheses located all the non-hydrogen atoms. The structure was refined on  $|F|$  by full-matrix anisotropic least squares. A difference synthesis enabled most of the H atoms to be located. Those of the methyl groups, C(26) and C(27), were poorly defined and their coordinates were determined geometrically with respect to a minimum energy conformation of the methyl groups.

The H atoms were subjected to isotropic refinement. However, the results for the C(26) and C(27) methyl groups produced unacceptable C-H lengths and abnormally large temperature factors. It is probable that some disorder exists in this region of the molecule, and, consequently, not too great a reliance can be placed on the parameters of these H atoms. A satisfactory weighting scheme was obtained with the equation  $w^{-1} = a + |F_o| + b|F_o|^2 + c|F_o|^3$  where  $a = 13.2$ ,  $b = -0.0343$  and  $c = 0.00078$ .

Corrections for anomalous dispersion were applied to all atoms, and the refinement converged to an  $R$  of 3.4% ( $R_w = 4.7\%$ ). The final scale factor for  $|F_o|$  was 0.977 (2). Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Computations were performed by local programs and the X-RAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The atomic parameters are listed in Table 3 and bond lengths and angles in Table 4.\*

#### Absolute configuration

The absolute configuration was examined by carrying out a least-squares refinement in the manner described above, but with the sign of the imaginary components

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31423 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

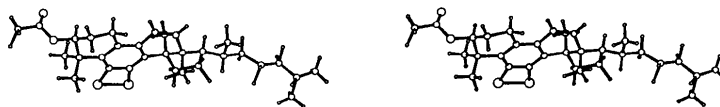


Fig. 1. Stereo view of the molecule, as seen along  $[0\bar{2}1]$ .

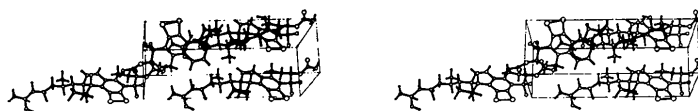


Fig. 2. Stereo view of molecular packing, as seen along  $[02\bar{1}]$ .

Table 4. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

S(1)—S(2)	2.119 (1)	O(1)—C(3)—C(2)	108.8 (3)
S(1)—C(7)	1.767 (4)	C(3)—C(4)	1.532 (6)
S(2)—C(6)	1.782 (4)	O(1)—C(3)—C(4)	109.3 (3)
O(1)—C(3)	1.462 (5)	C(2)—C(3)—C(4)	112.1 (3)
O(1)—C(31)	1.349 (5)	C(3)—H(31)	0.97 (4)
C(3)—O(1)—C(31)	118.0 (3)	O(1)—C(3)—H(31)	112 (2)
O(2)—C(31)	1.192 (6)	C(2)—C(3)—H(31)	110 (2)
C(1)—C(2)	1.523 (6)	C(4)—C(3)—H(31)	105 (2)
C(1)—C(10)	1.511 (6)	C(4)—C(5)	1.528 (5)
C(2)—C(1)—C(10)	113.4 (3)	C(3)—C(4)—C(5)	108.1 (3)
C(1)—H(11)	1.11 (4)	C(4)—C(29)	1.534 (6)
C(2)—C(1)—H(11)	111 (2)	C(3)—C(4)—C(29)	108.5 (3)
C(10)—C(1)—H(11)	110 (2)	C(5)—C(4)—C(29)	111.0 (3)
C(1)—H(12)	0.95 (5)	C(4)—C(30)	1.539 (6)
C(2)—C(1)—H(12)	111 (3)	C(3)—C(4)—C(30)	111.6 (3)
C(10)—C(1)—H(12)	103 (3)	C(5)—C(4)—C(30)	108.4 (3)
H(11)—C(1)—H(12)	107 (4)	C(29)—C(4)—C(30)	109.1 (4)
C(2)—C(3)	1.506 (6)	C(5)—C(6)	1.381 (5)
C(1)—C(2)—C(3)	109.0 (3)	C(4)—C(5)—C(6)	121.6 (3)
C(2)—H(21)	0.95	C(5)—C(10)	1.414 (5)
C(1)—C(2)—H(21)	111 (3)	C(4)—C(5)—C(10)	123.2 (3)
C(3)—C(2)—H(21)	114 (3)	C(6)—C(5)—C(10)	115.2 (3)
C(2)—H(22)	0.94 (4)	S(2)—C(6)—C(5)	135.7 (3)
C(1)—C(2)—H(22)	105 (2)	C(6)—C(7)	1.387 (5)
C(3)—C(2)—H(22)	113 (2)	S(2)—C(6)—C(7)	100.5 (3)
H(21)—C(2)—H(22)	105 (4)	C(5)—C(6)—C(7)	123.8 (4)
C(8)—C(9)	1.405 (5)	S(1)—C(7)—C(6)	103.3 (3)
C(7)—C(8)—C(9)	116.1 (3)	C(7)—C(8)	1.381 (5)
C(8)—C(14)	1.516 (5)	S(1)—C(7)—C(8)	134.5 (3)
C(7)—C(8)—C(14)	125.1 (3)	C(6)—C(7)—C(8)	122.1 (3)
C(9)—C(8)—C(14)	118.5 (3)	C(8)—C(14)—C(13)	108.8 (3)
C(9)—C(10)	1.425 (5)	C(14)—C(15)	1.536 (6)
C(8)—C(9)—C(10)	121.6 (3)	C(8)—C(14)—C(15)	118.9 (3)
C(9)—C(11)	1.470 (6)	C(13)—C(14)—C(15)	102.0 (3)
C(8)—C(9)—C(11)	117.1 (3)	C(14)—C(28)	1.543 (6)
C(10)—C(9)—C(11)	121.3 (3)	C(8)—C(14)—C(28)	105.7 (3)
C(1)—C(10)—C(5)	121.1 (3)	C(13)—C(14)—C(28)	113.7 (3)
C(1)—C(10)—C(9)	117.9 (3)	C(15)—C(14)—C(28)	108.0 (3)
C(5)—C(10)—C(9)	121.1 (3)	C(15)—C(16)	1.559 (6)
C(11)—C(12)	1.349 (6)	C(14)—C(15)—C(16)	102.3 (3)
C(9)—C(11)—C(12)	122.3 (4)	C(15)—H(151)	1.03 (5)
C(11)—H(111)	1.02 (5)	C(14)—C(15)—H(151)	113 (3)
C(9)—C(11)—H(111)	117 (3)	C(16)—C(15)—H(151)	108 (3)
C(12)—C(11)—H(111)	121 (3)	C(15)—H(152)	1.05 (5)
C(12)—C(13)	1.507 (6)	C(14)—C(15)—H(152)	114 (3)
C(11)—C(12)—C(13)	119.2 (4)	C(16)—C(15)—H(152)	106. (3)
C(12)—H(121)	0.95 (6)	H(151)—C(15)—H(152)	112 (4)
C(11)—C(12)—H(121)	122 (4)	C(16)—C(17)	1.539 (7)
C(13)—C(12)—H(121)	118 (4)	C(15)—C(16)—C(17)	108.4 (4)
C(13)—C(14)	1.555 (5)	C(16)—H(161)	0.96 (5)
C(12)—C(13)—C(14)	107.2 (3)	C(15)—C(16)—H(161)	109 (3)
C(13)—C(17)	1.565 (6)	C(17)—C(16)—H(161)	109 (3)
C(12)—C(13)—C(17)	119.9 (3)	C(16)—H(162)	1.22 (6)
C(14)—C(13)—C(17)	100.7 (3)	C(15)—C(16)—H(162)	114 (3)
		C(17)—C(16)—H(162)	112 (3)
		H(161)—C(16)—H(162)	104 (4)
		C(13)—C(17)—C(16)	102.4 (3)
		C(17)—C(20)	1.535 (6)
		C(13)—C(17)—C(20)	117.6 (4)
		C(16)—C(17)—C(20)	112.4 (4)

Table 4 (cont.)

C(13)—C(18)	1.532 (6)	C(17)—H(171)	1.01 (5)
C(12)—C(13)—C(18)	107.5 (3)	C(13)—C(17)—H(171)	112 (3)
C(14)—C(13)—C(18)	111.1 (3)	C(16)—C(17)—H(171)	109 (3)
C(17)—C(13)—C(18)	110.2 (3)	C(20)—C(17)—H(171)	104 (3)
C(18)—H(181)	1.09 (6)	C(23)—C(24)	1.507 (9)
C(13)—C(18)—H(181)	112 (3)	C(22)—C(23)—C(24)	114.6 (5)
C(18)—H(182)	0.91 (8)	C(23)—H(231)	0.94 (10)
C(13)—C(18)—H(182)	104 (4)	C(22)—C(23)—H(231)	106 (7)
H(181)—C(18)—H(182)	106 (6)	C(24)—C(23)—H(231)	135 (7)
C(18)—H(183)	1.04 (5)	C(23)—H(232)	1.32 (11)
C(13)—C(18)—H(183)	109 (3)	C(22)—C(23)—H(232)	96 (5)
H(181)—C(18)—H(183)	117 (4)	C(24)—C(23)—H(232)	102 (5)
H(182)—C(18)—H(183)	106 (5)	H(231)—C(23)—H(232)	91 (8)
C(20)—C(21)	1.605 (11)	C(24)—C(25)	1.501 (10)
C(17)—C(20)—C(21)	113.3 (5)	C(23)—C(24)—C(25)	116.3 (6)
C(20)—C(22)	1.541 (7)	C(24)—H(241)	0.89 (6)
C(17)—C(20)—C(22)	110.6 (4)	C(23)—C(24)—H(241)	120 (4)
C(21)—C(20)—C(22)	110.2 (5)	C(25)—C(24)—H(241)	121 (4)
C(20)—H(201)	1.08 (7)	C(24)—H(242)	1.24 (20)
C(17)—C(20)—H(201)	106 (4)	C(23)—C(24)—H(242)	85 (8)
C(21)—C(20)—H(201)	104 (4)	C(25)—C(24)—H(242)	108 (8)
C(22)—C(20)—H(201)	113 (4)	H(241)—C(24)—H(242)	91 (9)
C(21)—H(211)	1.07 (7)	C(25)—C(26)	1.428 (15)
C(20)—C(21)—H(211)	109 (3)	C(24)—C(25)—C(26)	114.7 (10)
C(21)—H(212)	1.09 (7)	C(25)—C(27)	1.531 (16)
C(20)—C(21)—H(212)	111 (4)	C(24)—C(25)—C(27)	107.1 (8)
H(211)—C(21)—H(212)	113 (5)	C(26)—C(25)—C(27)	99.5 (12)
C(21)—H(213)	0.89 (10)	C(25)—H(251)	1.40 (10)
C(20)—C(21)—H(213)	117 (7)	C(24)—C(25)—H(251)	99 (5)
H(211)—C(21)—H(213)	110 (8)	C(26)—C(25)—H(251)	135 (5)
H(212)—C(21)—H(213)	97 (7)	C(27)—C(25)—H(251)	98 (5)
C(22)—C(23)	1.515 (9)	C(28)—H(281)	1.02 (5)
C(20)—C(22)—C(23)	113.3 (5)	C(14)—C(28)—H(281)	111 (3)
C(22)—H(221)	1.03 (8)	C(28)—H(282)	1.02 (6)
C(20)—C(22)—H(221)	99 (5)	C(14)—C(28)—H(282)	107 (3)
C(23)—C(22)—H(221)	118 (4)	H(281)—C(28)—H(282)	102 (4)
C(22)—H(222)	0.95 (6)	C(28)—H(283)	1.01 (5)
C(20)—C(22)—H(222)	115 (4)	C(14)—C(28)—H(283)	111 (3)
C(23)—C(22)—H(222)	103 (4)	H(281)—C(28)—H(283)	114 (4)
H(221)—C(22)—H(222)	110 (6)	H(282)—C(28)—H(283)	112 (4)
C(29)—H(291)	0.96 (6)	C(31)—O(2)	1.192 (6)
C(4)—C(29)—H(291)	114 (3)	O(1)—C(31)—O(2)	123.8 (4)
C(29)—H(292)	0.95 (5)	C(31)—C(32)	1.504 (6)
C(4)—C(29)—H(292)	112 (3)	O(1)—C(31)—C(32)	110.2 (4)
H(291)—C(29)—H(292)	104 (5)	O(2)—C(31)—C(32)	126.0 (4)
C(29)—H(293)	1.01 (6)		
C(4)—C(29)—H(293)	109 (4)	C(32)—H(321)	1.20 (13)
H(291)—C(29)—H(293)	103 (5)	C(31)—C(32)—H(321)	114 (6)
H(292)—C(29)—H(293)	115 (5)	C(32)—H(322)	0.99 (6)
		C(31)—C(32)—H(322)	113 (4)
C(30)—H(301)	0.97 (5)	H(321)—C(32)—H(322)	89 (6)
C(4)—C(30)—H(301)	115 (3)	C(32)—H(323)	0.86 (8)
C(30)—H(302)	1.00 (4)	C(31)—C(32)—H(323)	111 (5)
C(4)—C(30)—H(302)	111 (2)	H(321)—C(32)—H(323)	128 (8)
H(301)—C(30)—H(302)	105 (4)	H(322)—C(32)—H(323)	98 (6)
C(30)—H(303)	1.05 (6)		
C(4)—C(30)—H(303)	107 (3)		
H(301)—C(30)—H(303)	112 (4)		
H(302)—C(30)—H(303)	107 (4)		

$\Delta f''$  reversed. Convergence was reached at  $R=3.6\%$ ,  $R_w=4.9\%$ . The ratio of the weighted  $R$  values is 1.04, and by Hamilton's ratio test (Hamilton, 1965) this result is significant at a level better than 0.01. The absolute configuration is given by the coordinates listed in Table 3 and corresponds, not surprisingly, with the 3-acetoxy group in the  $\beta$ -configuration.

### Discussion

Fig. 1 is a stereoscopic illustration of (I) as seen along  $[021]$ . The central ring system shows a considerable degree of planarity. Least-squares planes of interest, with atom deviations, are listed in Table 5. The two planes made by C(6) and C(7) with the two S atoms are

nearly coplanar (dihedral angle 0.35°), yet the slightly different environments of the two S atoms are revealed by the deviations from plane 1 (Table 5) and the different S-C-C angles (Table 4).

The angle between the planar acetate group (plane 4) and that of the central ring system (plane 1) is nearly 90°, a not uncommon feature in 3 $\beta$ -acetoxy steroids.

An interesting question turned upon the existence of the two S atoms as either a dithione (VIII) or a dithiete (IX). This problem has been clearly resolved, both from the geometry of the epidithio ring system (Table 4) and by Raman spectroscopy.

#### Raman spectrum

The crystalline solid was examined as a pressed powder at about 45° incidence to yellow (5682 Å) excitation. The sample was strongly fluorescent, but after about one hour the fluorescence fell by about 80%. The spectrum showed one Raman band at about 486 cm<sup>-1</sup>, which corresponds to the -S-S- stretch (Cymerman & Willis, 1951). The >C=S frequency is in the region of 1171-1180 cm<sup>-1</sup>. The dithiete formulation is regarded as confirmed.

Undoubtedly, *pd*-orbital overlap is partly responsible for the cohesion of the S-S bond. This mechanism is not possible for the smaller O species, and *o*-quinones containing >C=O, are well established. Attempts to prepare 1,2-dithiobenzene (Kusters & de Mayo, 1974) led to the dimer (X). Fig. 2 shows a molecular packing

Table 5. *Least-squares planes*

In these equations *X*, *Y* and *Z* are in Å, with *X*||*a*, *Y*⊥*ac* plane and *Z*⊥*a* in the *ac* plane.

Plane 1: C(5), C(6), C(7), C(8), C(9), C(10)

$$-0.2083X + 0.7885Y + 0.5787Z = 5.0719$$

<i>A</i>		<i>A</i>	
C(5)	0.011 Å	S(1)	-0.00 Å
C(6)	0.008	S(2)	0.05
C(7)	-0.019	C(1)	-0.07
C(8)	0.010	C(4)	0.04
C(9)	0.009	C(11)	0.05
C(10)	-0.019	C(14)	0.20

Plane 2: C(31), C(32), O(1), O(2)

$$0.3094X - 0.5274Y + 0.7913Z = 0.0629$$

<i>A</i>		<i>A</i>	
C(31)	0.005 Å	C(3)	0.03 Å
C(32)	-0.001		
O(1)	-0.001		
O(2)	-0.002		

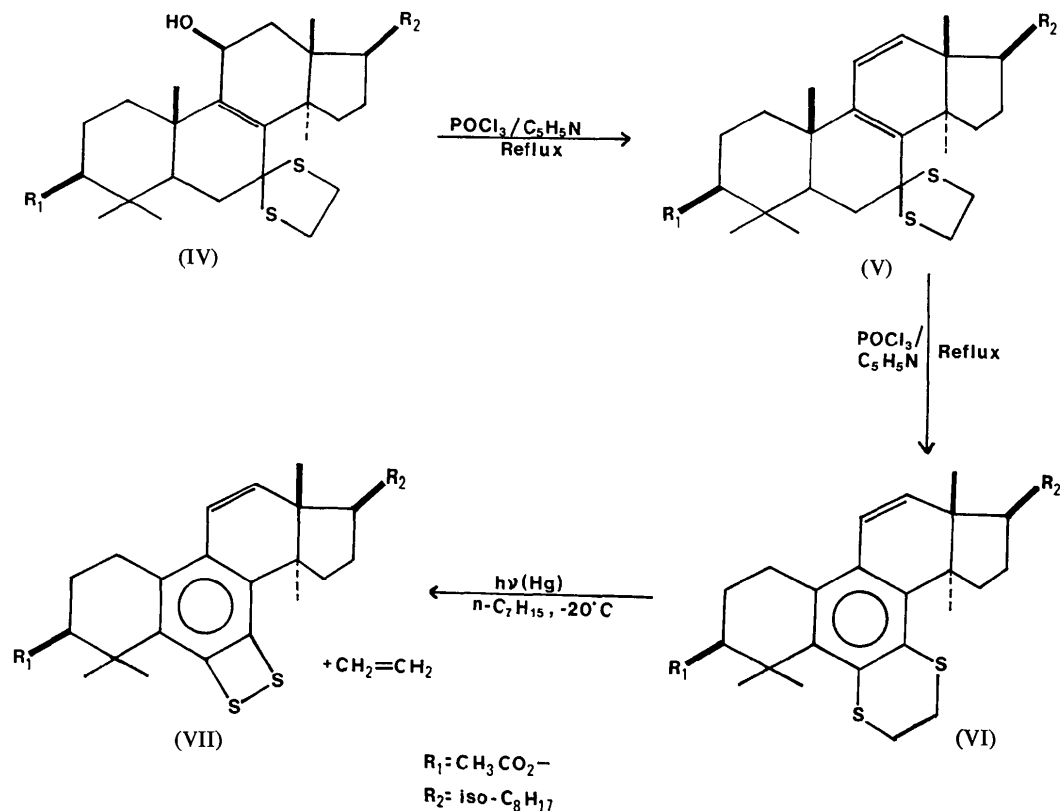
Plane 3: S(1), C(6), C(7)

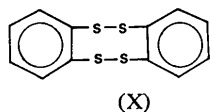
$$-0.1866X + 0.7869Y + 0.5882Z = 5.1387$$

Plane 4: S(2), C(6), C(7)

$$-0.1850X + 0.7837Y + 0.5930Z = 5.1241$$

diagram of (I). The intermolecular S...S distances are about 10 Å. There is no indication of a tendency towards dimerization. This is probably more likely to arise from steric factors preventing a sufficiently close approach of two molecules than from any particular stability conferred by the triterpenoid ring system.





In reactions of (IV) to (VII), or (I), stage (IV) to (V) gave the expected elimination of water with the formation of the 11,12 double bond. (V) to (VI) was accompanied by the loss of  $-\text{CH}_3$  and three other H atoms. In the final stage (VI) to (VII), the conversion was accompanied by loss of ethylene, found by g.l.c. analysis of the dibromide (Boar *et al.*, 1975).

From the known structure of (VII) it is reasonable to suggest that the mechanism of the subsequent reaction is first a disruption at the spiro-C(7), followed by migration of a S atom to C(6), with subsequent aromatization of ring B. The aromatization provides a conformational driving force for the elimination of the C(19) methyl group. Under the influence of UV activa-

tion, the structure is further stabilized by loss of ethylene from the dithian ring.

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## Structure Cristalline et Moléculaire à $-150^\circ\text{C}$ de la Diisopropyl-3,4 $\Delta$ 4-Thiazoline Thione-2

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The crystal and molecular structure of the compound  $\text{C}_9\text{H}_{15}\text{S}_2\text{N}$  has been determined by three dimensional analysis of X-ray diffraction. Crystals are monoclinic ( $P2_1/n$ ) and the unit cell has the dimensions  $a=7.771$ ,  $b=10.990$ ,  $c=12.220$  Å and  $\beta=91.89^\circ$ . The structure was solved by the heavy-atom method and refined by full-matrix least squares to  $R=0.034$  for 3007 independent X-ray reflexions measured with an automatic diffractometer (Nonius CAD-4) at low temperature ( $-150^\circ\text{C}$ ). The thiazoline ring is planar and the conformation of the isopropyl groups is largely controlled by intramolecular interactions.

### Introduction

La détermination de cette structure a été entreprise dans un contexte plus général qui concerne l'influence des effets stériques sur les réactions chimiques, en particulier, sur les dérivés de la  $\Delta$ 4-thiazoline thione-2 différemment substituée sur les positions 3, 4 et 5 (Fig. 1), où l'effet stérique est transmis par un engrangement des différents substituants (Roussel, 1973) sur le cycle thiazolinique. Cela rend sensible la réactivité de l'atome de soufre exocyclique à la nature du sub-

stituant alkyle qui se trouve sur la position 5, tout le reste de la molécule étant par ailleurs identique.

Une géométrie précise de dérivés de la  $\Delta$ 4-thiazoline thione-2 différemment substitués doit permettre de comprendre ce phénomène à partir des modifications de géométrie que subit la molécule lorsque l'un des substituants est changé. Il est évident qu'il est important d'évaluer l'incidence de l'état cristallin sur la géométrie moléculaire avant d'extrapoler cette dernière à la compréhension de phénomènes réactionnels qui se passent en solution.