

structure is not the orientation predicted on the basis of the biological data. This contradiction may arise because the bioassays measure several parameters including absorption, transport, and solubility properties in addition to affinities for intracellular receptors. Consequently, a complete understanding of the molecular features required for maximal glucocorticoid activity must await the availability of more complete data concerning the binding of these hormones to individual proteins.

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### 9-Carbomethoxy-4,6,6-trimethyl-*trans*-decal-3-one\*

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**Abstract.**  $C_{15}H_{24}O_3$ , triclinic, space group  $P\bar{1}$ ;  $a = 8.082$  (1),  $b = 14.398$  (2),  $c = 6.976$  (1) Å,  $\alpha = 111.64$  (1),  $\beta = 103.01$  (1),  $\gamma = 71.23$  (1)°,  $V = 709.27$  Å<sup>3</sup>, based on  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å.  $D_m = 1.180$ ,  $D_c = 1.181$  g cm<sup>-3</sup>,  $Z = 2$ ,  $\mu(\text{Mo } K\alpha) = 0.86$  cm<sup>-1</sup>,  $M = 252.34$ ,  $F(000) = 276$ . The ring junction is *trans*, with both rings in chair con-

formation. The methyl group attached to the cyclohexanone ring is equatorial, and the methyl ester at the ring junction is axial.

**Experimental.** The colourless prismatic crystals of this compound were supplied by Dr J. W. ApSimon of Carleton University. Initial precession photographs indicated that the symmetry was triclinic, and subse-

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Table 1. Fractional coordinates, vibration tensor components (Å<sup>2</sup>) for the expression  $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$ , and their e.s.d.'s, all  $\times 10^4$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	7083 (2)	7890 (1)	-326 (3)	351 (7)	522 (8)	608 (9)	562 (15)	110 (13)	-235 (12)
C(2)	7096 (2)	8588 (1)	1937 (3)	443 (8)	592 (9)	602 (10)	491 (16)	-179 (14)	-465 (14)
C(3)	5342 (2)	9374 (1)	2303 (2)	573 (9)	468 (8)	361 (7)	333 (12)	-132 (12)	-393 (14)
C(4)	3770 (2)	8927 (1)	1664 (2)	423 (7)	370 (7)	349 (7)	186 (11)	34 (11)	-173 (11)
C(5)	2199 (2)	7781 (1)	-1520 (2)	327 (6)	430 (7)	343 (7)	178 (11)	111 (10)	-150 (11)
C(6)	2141 (2)	7174 (1)	-3854 (2)	396 (7)	455 (8)	347 (7)	185 (11)	34 (11)	-214 (11)
C(7)	3901 (2)	6348 (1)	-4259 (2)	517 (8)	412 (8)	359 (7)	88 (12)	148 (12)	-85 (12)
C(8)	5491 (2)	6785 (1)	-3399 (2)	414 (7)	498 (8)	376 (7)	282 (12)	252 (11)	2 (12)
C(9)	5559 (2)	7372 (1)	-1043 (2)	331 (6)	382 (7)	359 (7)	287 (11)	131 (10)	-124 (10)
C(10)	3803 (2)	8222 (1)	-637 (2)	338 (6)	339 (6)	328 (6)	237 (10)	70 (10)	-102 (10)
O(11)	5214 (2)	10296 (1)	3019 (2)	861 (9)	467 (6)	601 (7)	336 (11)	-115 (13)	-582 (12)
C(12)	2066 (2)	9776 (1)	2063 (3)	512 (9)	499 (9)	519 (10)	-51 (15)	86 (15)	-2 (15)
C(13)	649 (3)	6637 (2)	-4508 (3)	601 (11)	730 (12)	506 (9)	157 (17)	-51 (15)	-670 (18)
C(14)	1786 (2)	7902 (1)	-5125 (2)	497 (8)	606 (9)	399 (8)	398 (14)	11 (13)	-114 (14)
C(15)	5878 (2)	6599 (1)	111 (2)	374 (6)	365 (7)	383 (7)	277 (11)	47 (10)	-166 (10)
O(16)	4941 (2)	6598 (1)	1210 (2)	643 (7)	602 (7)	735 (8)	770 (13)	579 (13)	7 (11)
O(17)	7397 (1)	5868 (1)	-258 (2)	441 (6)	531 (7)	824 (8)	793 (12)	326 (11)	93 (10)
C(18)	7810 (2)	5088 (1)	739 (3)	525 (9)	517 (9)	869 (13)	832 (19)	36 (17)	-119 (15)

quently cell parameters and intensity data were measured on a Picker diffractometer, with graphite-monochromatized Mo  $K\alpha$  radiation. A crystal with approximate dimensions  $0.3 \times 0.4 \times 0.5$  mm was mounted in a random orientation, and cell parameters were obtained from angular measurements of 26 reflexions with  $2\theta$  between  $36$  and  $48^\circ$ . The intensities of 3287 unique reflexions in the hemisphere with  $2\theta \leq 55^\circ$ , were measured by the  $\theta/2\theta$  scan technique. The scan range,  $\Delta 2\theta^\circ$ , was of the form  $\Delta 2\theta = 0.6 + 0.69 \tan \theta + 0.7$  and background measurements of 20 s were taken at both ends of this range. Three reflexions were monitored every 25 measurements, and these reference measurements were later used to place all intensities on the same scale. 613 reflexions which had net counts  $< 1.5 \sigma(I)$  were not used for the analysis. Absorption corrections were not applied ( $\mu = 0.86 \text{ cm}^{-1}$ ).

Table 2. Hydrogen atom parameters and their e.s.d.'s

	Positional parameters are $\times 10^3$ .			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
H(11)	693 (2)	831 (1)	-121 (3)	4.0 (0.4)
H(12)	822 (2)	735 (1)	-54 (3)	4.1 (0.4)
H(21)	804 (3)	892 (1)	232 (3)	4.6 (0.4)
H(22)	729 (3)	815 (1)	284 (3)	4.6 (0.4)
H(41)	397 (2)	849 (1)	253 (3)	3.2 (0.3)
H(51)	218 (2)	733 (1)	-74 (3)	3.5 (0.3)
H(52)	112 (2)	834 (1)	-130 (3)	3.7 (0.4)
H(71)	389 (2)	600 (1)	-579 (3)	4.3 (0.4)
H(72)	399 (2)	580 (1)	-362 (3)	4.0 (0.4)
H(81)	551 (2)	728 (1)	-407 (3)	3.7 (0.4)
H(82)	660 (3)	624 (2)	-367 (3)	4.5 (0.4)
H(101)	375 (2)	867 (1)	-141 (3)	3.2 (0.3)
H(121)	174 (3)	1012 (2)	102 (3)	5.9 (0.5)
H(122)	106 (3)	950 (2)	193 (3)	5.8 (0.5)
H(123)	210 (3)	1027 (2)	345 (4)	6.7 (0.6)
H(131)	77 (3)	616 (2)	-373 (3)	5.7 (0.5)
H(132)	-51 (3)	717 (2)	-420 (3)	5.9 (0.5)
H(133)	60 (3)	621 (2)	-593 (4)	6.2 (0.5)
H(141)	269 (3)	831 (2)	-477 (3)	5.4 (0.5)
H(142)	67 (3)	841 (2)	-486 (3)	4.8 (0.4)
H(143)	180 (3)	748 (2)	-659 (4)	6.0 (0.5)
H(181)	893 (3)	472 (2)	45 (4)	7.7 (0.6)
H(182)	695 (3)	471 (2)	22 (4)	6.6 (0.6)
H(183)	778 (3)	540 (2)	222 (4)	6.7 (0.6)

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966) in the centrosymmetric space group  $P\bar{1}$ . Refinement was by block-diagonal least-squares calculations, minimizing  $\sum \omega(|F_o| - |F_c|)^2$ . All the hydrogen atoms were clearly indicated on a difference map and their parameters were ultimately refined isotropically, while the other atoms were refined anisotropically. Scattering factor values for C and O were those of Hanson, Herman, Lea & Skillman (1964), and values for bonded H were taken from Stewart, Davidson & Simpson (1965). The final weighting scheme, chosen to minimize the dependence of  $\langle \omega \Delta^2 \rangle$  on  $|F_o|$  and  $\sin^2 \theta$ , was of the form  $\omega = 1/[3.0 + |F_o| + 0.02|F_o|^2]$ . Five strong reflexions which appear to be affected by extinction were given zero weight during the final refinement cycles. The final *R* value ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) was 0.046 for all observed reflexions.

A difference map calculated from the final structure factors\* showed 18 peaks over  $0.12 \text{ e \AA}^{-3}$  in height; the estimated standard deviation of the electron density (Cruickshank, 1959) is  $0.040 \text{ e \AA}^{-3}$ . Eleven of these peaks are in positions consistent with bonding or lone-pair electron density, while the others are apparently spurious.

Final parameters and their e.s.d.'s are given in Tables 1 and 2 and a stereoscopic view of the molecule is shown in Fig. 1. Bond lengths, angles, and the numbering scheme are given in Fig. 2. The C-H bond distances vary from  $0.92$  to  $1.02 \text{ \AA}$ , with e.s.d.'s about  $0.02 \text{ \AA}$ . The anisotropic thermal parameters were analysed for rigid-body motion with the *MGTLS* program (Schomaker & Trueblood, 1968). However, even by considering various molecular fragments no satisfactory fit was obtained between the observed  $U_{ij}$ 's and those calculated from the translation and libration

\* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30514 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

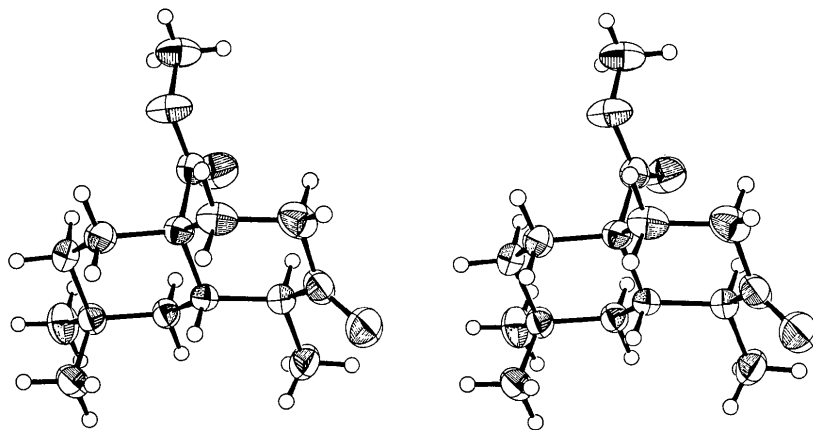


Fig. 1. Stereoscopic view of the molecule drawn by *ORTEP-II* (Johnson, 1971). The thermal vibration ellipsoids represent 50% probability.

Table 3. Torsional angles within the two rings

C(9)—C(1)—C(2)—C(3)	−54.2°	C(10)—C(5)—C(6)—C(7)	53.0°
C(1)—C(2)—C(3)—C(4)	54.5	C(5)—C(6)—C(7)—C(8)	−53.4
C(2)—C(3)—C(4)—C(10)	−53.9	C(6)—C(7)—C(8)—C(9)	56.8
C(3)—C(4)—C(10)—C(9)	54.7	C(7)—C(8)—C(9)—C(10)	−55.2
C(4)—C(10)—C(9)—C(1)	−56.1	C(8)—C(9)—C(10)—C(5)	54.7
C(10)—C(9)—C(1)—C(2)	55.0	C(9)—C(10)—C(5)—C(6)	−56.0

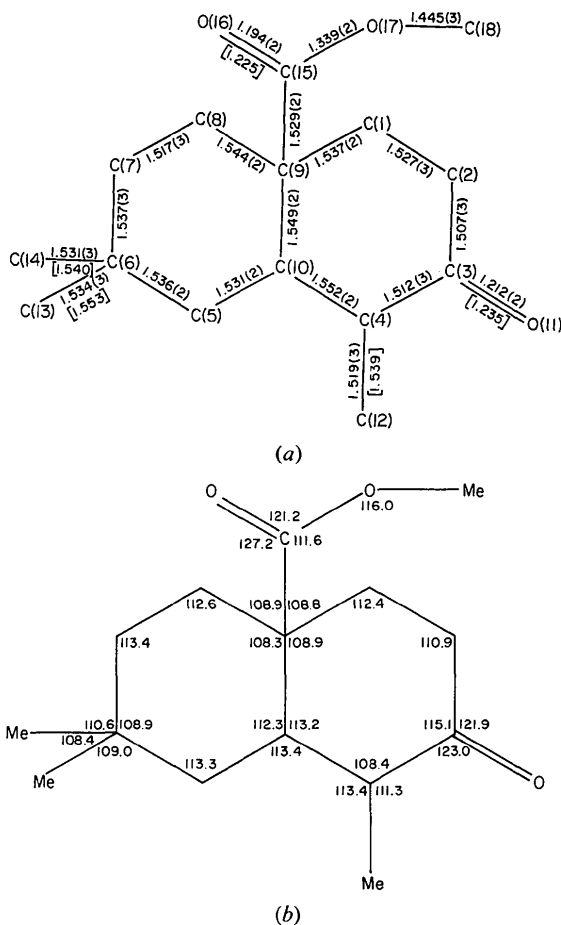


Fig. 2. (a) Bond lengths (Å) and numbering scheme. Riding-motion corrections have been applied to the bond length values in square brackets. (b) Bond angles (°). Angles not shown in the figure: C(5)—C(6)—C(14) 110.8; C(7)—C(6)—C(13) 109.1; C(8)—C(9)—C(1) 109.7; C(10)—C(9)—C(15) 112.2°. E.s.d.'s for the bond angles are 0.12–0.15°.

tensors. Consequently no libration corrections have been applied to the bond lengths. Riding motion corrections (Busing & Levy, 1964) have, instead, been calculated for the C(3)—O(11), C(4)—C(12), C(6)—C(13), C(6)—C(14) and C(15)—O(16) bonds, and these corrected bond lengths are also given in Fig. 2. The 'riding-motion' model was found to be inapplicable to O(17)—C(18).

The cell parameters were calculated and the intensity data collection was controlled by the computer programs of Gabe, Alexander & Goodman (1970). Other programs used in this determination were from the

NRC series of crystallographic programs (Ahmed, Hall, Pippy & Huber, 1973).

**Discussion.** This compound was synthesized as a possible precursor of several pentacyclic triterpenoids (Nguyen, 1972), and the X-ray analysis was undertaken to provide details of the stereochemistry. This analysis has established unexpectedly that the ring junction is *trans*. Both six-membered rings have the chair conformation. The observed torsional angles, given in Table 3, are 1.6° larger on average than those calculated theoretically for the cyclohexanone ring (Bucourt & Hainaut, 1967) and, on average, 2.2° less than calculated values (Bucourt & Hainaut, 1965) for a cyclohexane ring. The methyl group at C(4) is equatorial and the methyl ester group at C(9) is axial, with the C(10)—C(9)—C(15)—O(17) torsional angle = 180.2°. C(18) is within 0.02 Å of coplanarity with the C(9), C(15), O(16), O(17) plane. The carbonyl system at C(3) is significantly non-planar;  $\chi^2$  is 34.1 for the mean plane through C(2), C(3), C(4), O(11).

The structure is loosely packed with no hydrogen bonds, and none of the intermolecular contacts are shorter than the corresponding van der Waals distances.

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