observée (sauf celle des oxygènes centraux) correspond en fait à la superposition de deux pics atomiques trop proches l'un de l'autre pour être résolus.

On remarque que deux molécules possèdent pratiquement la même géométrie. Les distances de liaison et angles de valence sont donnés dans le Tableau 2. On obtient, malgré le désordre structural, des valeurs paraissant correctes sauf au niveau du centre de chaque molécule où la superposition des pics atomiques doit être moins bonne que pour les autres atomes. La moyenne des distances observées pour la liaison N=N: 1,254 Å, plus longue que celle trouvée dans le *para*-azoxyanisole (1,218 Å) (Krigbaum *et al.*, 1970) est proche de celle obtenue dans le *para*-azotoluène (1,243 Å) (Brown, 1966). Les distances N—O: 1,501 et 1,548 Å, paraissent anormalement grandes si on les compare respectivement aux valeurs: 1,279 et 1,31 Å, observées dans le *para*-azoxyanisole (Krigbaum *et al.*, 1970) et dans le *cis*-nitrosométhane (Germain, Piret & Van Meerssche, 1963). Les autres distances et angles sont au contraire identiques à ceux obtenus dans le *para*-azoxyanisole.

Les molécules sont toutes alignées suivant une même direction (approximativement {214}) (Figs. 1 et 2). Les plans moyens des deux molécules indépendantes font entre eux un angle de 63 (1)°. L'empilement moléculaire est semblable à celui rencontré dans les composés nématogènes de même type: *para*-azoxyanisole (Krigbaum *et al.*, 1970), anisaldéhyde-azine (Galigné & Falgueirettes, 1968), 4,4'-azodiphénétole (Galigné, 1970). Chaque molécule est entourée de 12 molécules voisines avec un empilement hexagonal dans le plan perpendiculaire à l'axe d'allongement.

Une étude de la variation du vecteur de modulation (phase I) en fonction de la température est en cours. Les résultats actuels manquet de précision et restent à vérifier. Il semblerait néanmoins qu'ily ait une très légère diminution de la composante du vecteur de modulation suivant a^* et une augmentation de celle suivant b^* lorsque la température décroit. Nous envisageons également une étude structurale de cette phase en utilisant l'approche quadridimensionnelle proposé par de Wolff (1974) puis complétée par de Wolff, Janssen & Janner (1981) et par Yamamoto (1982) pour les calculs de facteurs de structure et les affinements.

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Structure and Stereochemistry of Cacalone Acetate, a Sesquiterpene*

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Abstract. 3,4,5-Trimethyl-9-oxo-5,6,7,8-tetrahydro-4*H*-naphtho[2,3-*b*]furan-4-yl acetate, $C_{17}H_{20}O_4$, $M_r = 288{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}434\,(2)$, $b = 12{\cdot}009\,(4)$, $c = 19{\cdot}849\,(4)$ Å, $V = 1534\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}082$ mm^{-1}, $F(000) = 616$, $T = 293$ K, final $R = 0{\cdot}056$ for 1048 observed reflections. The X-ray analysis

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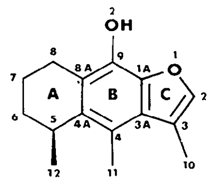
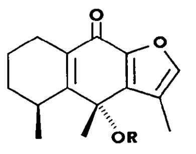
confirms the structure previously assigned on the basis of chemical and NMR studies. The stereochemistry at C(5) is 5(*S*). The *A* ring adopts a 1,2-diplanar conformation. The packing in the crystal is entirely due to intermolecular C—H···O contacts and van der Waals forces.

Introduction. Cacalol (1) and cacalone (2) are two sesquiterpenes which were isolated from the roots of *Cacalia decomposita* A. Gray, a shrub indigenous to northern Mexico (Romo & Joseph-Nathan, 1964). Chemical structures for (1) and (2) have evolved through a series of revisions (Joseph-Nathan, Morales & Romo, 1966; Kakisawa, Inouye & Romo, 1969; Brown & Thomson, 1969; Ruiz, Correa & Maldonado, 1969). More recently, the chemical structure of cacalone (2) was proposed based on the conversion of cacalone acetate (3) into cacalol (1) (Yuste, Díaz, Walls & Jankowski, 1976; Casares & Maldonado, 1976) and by ^{13}C and ^{1}H NMR spectroscopic studies (Jankowski, Díaz & Yuste, 1984).

The absolute configuration of cacalol was established to be 5(*S*) (Terabe, Tada & Takahashi, 1978) and the structure of cacalol methyl ether (Soriano-García, Walls, Barrios, Ortiz, Sánchez-Obregón, Toscano & Yuste, 1987) has been determined. The X-ray crystallographic structural determination of (3) was undertaken in order to understand the detailed geometry of this molecule.



(1)



(2) *R* = H
(3) *R* = CO–CH$_3$

Experimental. Yellow crystal, 0·20 × 0·34 × 0·34 mm. Nicolet *R*3 four-circle diffractometer, graphite-monochromatized Mo *K*α radiation. Lattice parameters from 25 machine-centred reflections with $5{\cdot}3 < 2\theta < 20{\cdot}9°$. 1590 reflections measured with $3 < 2\theta < 50°$ for one octant, of which 1048 had $I > 2{\cdot}5\sigma(I)$ and were used in the refinement. Index range *h* 0→7, *k* 0→13, *l* 0→23, $2\theta/\theta$ scan mode, variable scan speed, scan width 1·0° (θ). Two standard reflections (110, $\bar{1}0\bar{3}$) monitored every 50 measurements; no significant variation. Lp correction, absorption ignored and $R_{\rm int} = 0{\cdot}049$. Structure solved by direct methods using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms with anisotropic thermal parameters. The H atoms of CH, CH$_2$ and CH$_3$ groups were allowed to ride on bonded C. All H atoms assigned fixed isotropic temperature factor $U = 0{\cdot}06$ Å^2. $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}0011(F_o)^2]^{-1}$, where σ is the standard deviation of observed amplitudes based on counting statistics. In the last cycle $(\Delta/\sigma)_{\rm max} = 0{\cdot}038$; residual electron density within $-0{\cdot}19$ to $0{\cdot}22$ e Å^{-3}; $S = 1{\cdot}21$; final $R = 0{\cdot}056$ and $wR = 0{\cdot}062$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs.

Discussion. Fig. 1 shows the molecular conformation of (3). Final atomic coordinates are in Table 1* and bond distances and angles in Table 2.

The molecular structure of (3) determined from X-ray data confirms the structure previously assigned on the basis of chemical and spectroscopic methods and the stereochemistry at C(5) as 5(*S*).

The conformation of ring *A* may be described as a 1,2-diplanar conformation with C(6) 0·69 (7) Å out of the best plane formed by the other five ring atoms. This type of conformation occurs also in cacalol methyl ether (Soriano-García *et al.*, 1987).

The *B* ring to which the acetoxy and methyl groups are attached at C(4) shows a slight but significant deviation from planarity (r.m.s. deviation 0·076 Å). The acetoxy group is oriented to minimize transannular repulsions between the O atoms and the methyl substituents of both *A* and *C* rings. The pertinent torsion angles are C(3*A*)–C(4)–O(3)–C(13) = −63·6 (5) and C(4*A*)–C(4)–O(3)–C(13) = 61·9 (5)°. The C=O bond agrees with the accepted value of 1·215 (5) Å (Sutton, 1965). The *C* ring is planar within

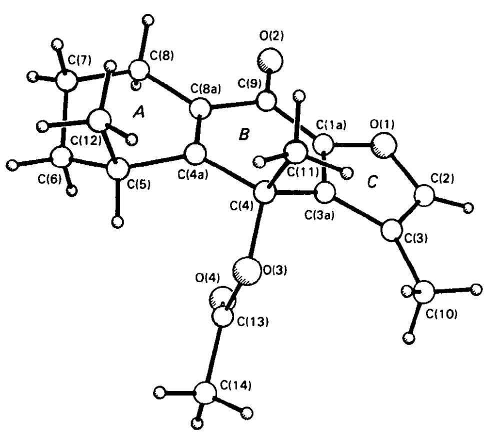


Fig. 1. The molecular structure of (3) showing the atom labelling.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and the results of mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44670 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
O(1)	8492 (6)	8389 (4)	2193 (2)	69 (1)
C(2)	7965 (10)	7507 (5)	1792 (3)	70 (2)
C(3)	6607 (9)	7804 (5)	1307 (3)	63 (2)
C(3a)	6228 (8)	8968 (4)	1410 (2)	51 (2)
C(4)	4732 (7)	9773 (4)	1102 (2)	47 (2)
C(4a)	5247 (7)	10984 (4)	1283 (2)	44 (2)
C(5)	4304 (9)	11901 (4)	846 (3)	62 (2)
C(6)	5641 (11)	12925 (5)	886 (3)	77 (2)
C(7)	5851 (11)	13312 (5)	1611 (3)	75 (2)
C(8)	6852 (10)	12431 (4)	2036 (3)	65 (2)
C(8a)	6428 (8)	11247 (4)	1822 (2)	51 (2)
C(9)	7561 (8)	10386 (5)	2213 (2)	57 (2)
C(9a)	7395 (8)	9272 (4)	1944 (2)	53 (2)
C(10)	5727 (12)	7054 (5)	781 (4)	98 (3)
C(11)	2521 (8)	9445 (5)	1338 (3)	68 (2)
C(12)	2009 (9)	12154 (5)	1012 (3)	86 (2)
O(2)	8616 (7)	10620 (4)	2708 (2)	84 (2)
O(3)	4618 (5)	9623 (3)	371 (2)	54 (1)
C(13)	6360 (9)	9822 (4)	8 (2)	51 (2)
O(4)	7981 (5)	10094 (3)	250 (2)	67 (1)
C(14)	5943 (11)	9667 (5)	−726 (2)	74 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(2)	1·368 (7)	O(1)—C(9a)	1·366 (7)
C(2)—C(3)	1·348 (8)	C(3)—C(3a)	1·434 (8)
C(3)—C(10)	1·490 (9)	C(3a)—C(4)	1·496 (7)
C(3a)—C(9a)	1·348 (7)	C(4)—C(4a)	1·534 (7)
C(4)—C(11)	1·549 (7)	C(4)—O(3)	1·464 (5)
C(4a)—C(5)	1·527 (7)	C(4a)—C(8a)	1·350 (6)
C(5)—C(6)	1·503 (8)	C(5)—C(12)	1·543 (8)
C(6)—C(7)	1·517 (8)	C(7)—C(8)	1·499 (8)
C(8)—C(8a)	1·508 (7)	C(8a)—C(9)	1·484 (7)
C(9)—C(9a)	1·444 (8)	C(9)—O(2)	1·227 (6)
O(3)—C(13)	1·353 (6)	C(13)—O(4)	1·193 (6)
C(13)—C(14)	1·494 (6)		

C(2)—O(1)—C(9a)	105·2 (4)	O(1)—C(2)—C(3)	111·8 (5)
C(2)—C(3)—C(3a)	105·4 (5)	C(2)—C(3)—C(10)	125·9 (5)
C(3a)—C(3)—C(10)	128·7 (5)	C(3)—C(3a)—C(4)	132·9 (5)
C(3)—C(3a)—C(9a)	106·4 (5)	C(4)—C(3a)—C(9a)	120·4 (5)
C(3a)—C(4)—C(4a)	112·2 (4)	C(3a)—C(4)—C(11)	107·6 (4)
C(4a)—C(4)—C(11)	111·7 (4)	C(3a)—C(4)—O(3)	111·0 (4)
C(4a)—C(4)—O(3)	111·1 (4)	C(11)—C(4)—O(3)	102·8 (4)
C(4)—C(4a)—C(5)	117·7 (4)	C(4)—C(4a)—C(8a)	122·0 (4)
C(5)—C(4a)—C(8a)	120·3 (4)	C(4a)—C(5)—C(6)	109·4 (5)
C(4a)—C(5)—C(12)	113·7 (4)	C(6)—C(5)—C(12)	112·0 (5)
C(5)—C(6)—C(7)	110·6 (5)	C(6)—C(7)—C(8)	110·8 (5)
C(7)—C(8)—C(8a)	115·4 (5)	C(4a)—C(8a)—C(8)	123·0 (5)
C(4a)—C(8a)—C(9)	121·8 (5)	C(8)—C(8a)—C(9)	114·9 (4)
C(8a)—C(9)—C(9a)	114·6 (4)	C(8a)—C(9)—O(2)	122·0 (5)
C(9a)—C(9)—O(2)	123·3 (5)	O(1)—C(9a)—C(3a)	111·2 (5)
O(1)—C(9a)—C(9)	123·2 (4)	C(3a)—C(9a)—C(9)	125·6 (5)
C(4)—O(3)—C(13)	117·6 (4)	O(3)—C(13)—O(4)	124·0 (4)
O(3)—C(13)—C(14)	110·3 (5)	O(4)—C(13)—C(14)	125·7 (5)

the limits of experimental error with maximum deviations of −0·002 (7) and 0·002 (7) Å at C(2) and C(3), respectively. The angle between the best planes through the *B* and *C* rings is 5·4 (7)°.

The arrangement of the molecules in the unit cell is shown in Fig. 2. Excluding H atoms there are three intermolecular approaches <3·4 Å, C(11)···O(1) $(-1+x,y,z)$ 3·35 (1), C(2)···O(2) $(2-x, -0.5+y, 0.5-z)$ 3·31 (1) and C(14)···O(2) $(1.5-x, 2-y, -0.5+z)$ 3·14 (1) Å. No suitable H donors for H-bond formation are available. The molecules are held in the crystal by van der Waals forces.

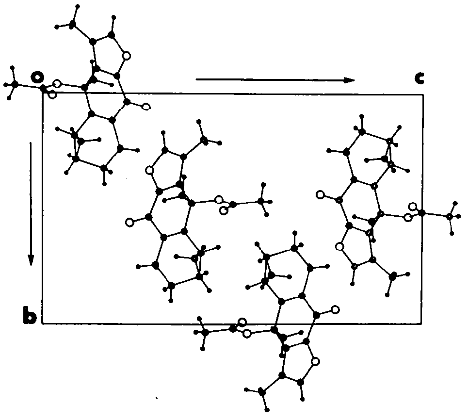

Fig. 2. Packing arrangement as viewed along **a**.

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