

## ORGANIC COMPOUNDS

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**(1 $\alpha$ ,3 $\alpha$ ,11 $\alpha$ )-2,2,11-Trimethyl-14-oxatetracyclo[6.5.0.1<sup>7,11</sup>.0<sup>3,8</sup>]tetradec-6-ene-5,9-dione**

V. KABALEESWARAN,<sup>a</sup> S. S. RAJAN,<sup>a</sup> G. P. KALENA,<sup>b</sup>  
P. PRADHAN<sup>b</sup> AND A. BANERJI<sup>b</sup>

<sup>a</sup>*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India, and*

<sup>b</sup>*Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India*

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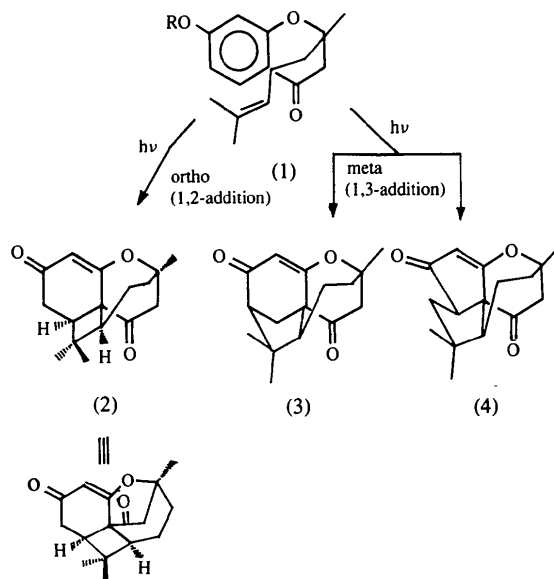
**Abstract**

The title compound, C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>, was prepared by the photolysis of 7-hydroxy-2-methyl-2-(4-methyl-3-pentenyl)-4-chromanone. The H7 and H9 atoms are in an  $\alpha$  configuration. The cyclobutane ring is non-planar, the cyclohexenone ring has a half-chair conformation, the pyranone ring has a sofa conformation and the cycloheptanone ring has a boat conformation. The groups of atoms C11, C12, C13, O14 and C12, C13, O14, C4 are both planar.

**Comment**

The photolysis of 7-hydroxy-2-methyl-2-(4-methyl-3-pentenyl)-4-chromanone, (1), gave a new class of tetracyclic compound (C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>) as a crystalline photo-product in 25% yield. Three possible structures, (2), (3) and (4), were considered for the photoproduct from the analysis of NMR, MS, IR and UV spectral data. The formation of (2) can be explained in terms of an intramolecular 1,2-arene-alkene photocycloaddition, while compounds (3) and (4) may be obtained by a 1,3-arene-alkene photocycloaddition. Detailed two-dimensional NMR studies in conjunction with base-catalyzed deuterium-exchange experiments supported structure (2) as the structure of the photoadduct. The relative stereochemistry of (2) was established from the two-dimensional spectrum (Kalena, Pradhan & Banerji, 1992). The X-ray investigation reported here provides independent confirmation of the structure of the photo-product as (1 $\alpha$ ,3 $\alpha$ ,11 $\alpha$ )-2,2,11-trimethyl-14-oxatetracyclo[6.5.0.1<sup>7,11</sup>.0<sup>3,8</sup>]tetradec-6-ene-5,9-dione, (2).

The title compound crystallizes in the centrosymmetric space group *C2/c*. The molecule has four asymmetric C atoms at C1, C4, C7 and C9, and Fig. 1 shows the molecule in the 1*R*,4*S*,7*S*,9*R* conformation. Atoms H7 and H9 are in an  $\alpha$  configuration, as expected from the spectral analysis (Kalena, Pradhan & Banerji, 1992); the dihedral angles are C13—C1—C7—H7 = -146 (1) and C13—C1—C9—H9 = 153 (1)°. The bond lengths



and angles around the tetrahedral C1 atom deviate from normal tetrahedral values and this may be attributed to the fusion of the four rings.

The cyclohexenone ring *A* is in a half-chair conformation ( $\Delta C_2 = 0.2^\circ$ ) in the crystal (Duax, Weeks & Rohrer, 1976). Atom O18 is displaced from the C11, C12, C13, C1 plane by -0.045 Å. Information on the stereodynamics of compound (2) in solution was obtained from high-resolution NMR studies at variable temperatures (298 → 233 K). The multiplicity of the signal for atoms H10A and H10B at the diastereotopic C10 atom ( $\delta$  2.35) changed from an *A*<sub>2</sub>*X* doublet (*J*<sub>AX</sub> = 4.7 Hz) at 298 K to an *ABX* doublet-quartet (*J*<sub>AB</sub> = 18.2, *J*<sub>AX</sub> = 6.6 and *J*<sub>BX</sub> = 2.2 Hz) at low temperature (233 K). The multiplicity of atom H9 also changed from triplet

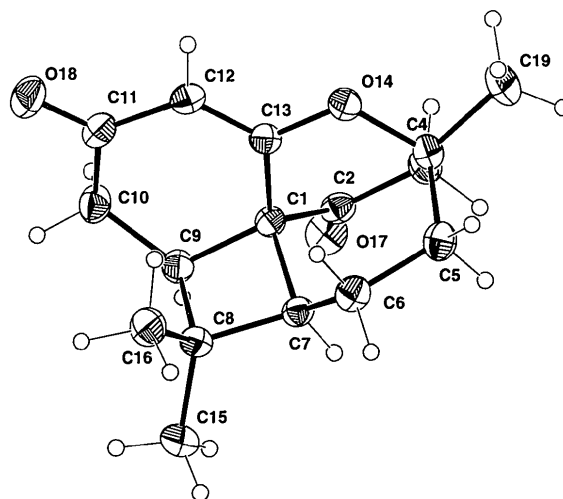


Fig. 1. A perspective view of the title molecule. Displacement ellipsoids are plotted at the 30% probability level.

(at 293 K) to double doublet (at 233 K). This indicated rapid interconversion of the possible conformers of the cyclohexanone ring in solution at 298 K, resulting in the equivalency of the protons of the methylene group. This equivalency was lost at lower temperature when the molecule acquired an energetically stable conformation. This conformation presumably is the same as that observed by X-ray crystallography. The pyranone ring *B* is in a sofa conformation ( $\Delta C_s = 3.0^\circ$ ) and the cycloheptanone ring *C* is in a boat conformation ( $\Delta C_s = 7.7^\circ$ ) (Bixon & Lifson, 1967). The cyclobutane ring *D* is not planar. Spectral studies indicated that a non-planar conformation of these rings is more favourable than a planar conformation (Rathjens, Freeman, Guinn & Pitzer, 1953). The average C—C bond length within the cyclobutane ring [1.563 (3) Å] is similar to values observed in other cyclobutane structures (Shirrell & Williams, 1973). The average C—C—C bond angle of the cyclobutane ring is 89.1 (1)°. Atom C8 is displaced by  $-0.38$  (2) Å from the C7, C1, C9 plane. The displacements of atoms H7 and H9 are 0.94 (2) and 0.90 (2) Å, respectively. The dihedral angles C11—C12—C13—O14 = 179 (2) and C12—C13—O14—C4 = 178 (2)° show the planarity of these groups. The molecules in the unit cell are stabilized by van der Waals interactions.

## Experimental

Crystals of (1 $\alpha$ ,3 $\alpha$ ,11 $\alpha$ )-2,2,11-trimethyl-14-oxatetracyclo-[6.5.0.1<sup>7,11</sup>.0<sup>3,8</sup>]tetradec-6-ene-5,9-dione were obtained from benzene. The density  $D_m$  was measured by flotation within KBr/H<sub>2</sub>O solution.

### Crystal data

C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>  
 $M_r = 260.3$   
 Monoclinic  
 C2/c  
 $a = 26.287$  (5) Å  
 $b = 7.440$  (2) Å  
 $c = 17.775$  (4) Å  
 $\beta = 127.64$  (2)°  
 $V = 2753$  (1) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.256$  Mg m<sup>-3</sup>  
 $D_m = 1.26$  (2) Mg m<sup>-3</sup>

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 empirical via  $\psi$  scan  
 (North, Phillips &  
 Mathews, 1968)  
 $T_{\min} = 0.96$ ,  $T_{\max} = 0.99$   
 2598 measured reflections  
 2442 independent reflections

Cu K $\alpha$  radiation  
 $\lambda = 1.5418$  Å  
 Cell parameters from 25  
 reflections  
 $\theta = 15$ – $25^\circ$   
 $\mu = 0.65$  mm<sup>-1</sup>  
 $T = 273$  K  
 Needle  
 $0.28 \times 0.13 \times 0.10$  mm  
 White  
 1969 observed reflections  
 $[I > 3\sigma(I)]$   
 $R_{\text{int}} = 0.03$   
 $\theta_{\text{max}} = 70^\circ$   
 $h = -31 \rightarrow 31$   
 $k = 0 \rightarrow 9$   
 $l = 0 \rightarrow 21$   
 3 standard reflections  
 monitored every 200  
 reflections  
 intensity decay: 2%

### Refinement

Refinement on  $F$   
 $R = 0.041$   
 $wR = 0.051$   
 $S = 0.75$   
 1969 reflections  
 172 parameters  
 All H-atom parameters  
 refined

$w = 1/[\sigma^2(F)$   
 $+ 0.007231(F)^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.03$   
 $\Delta\rho_{\text{max}} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.18$  e Å<sup>-3</sup>  
 Atomic scattering factors  
 from SHELXS86  
 (Sheldrick, 1985)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C1	0.3685 (1)	0.1302 (2)	0.4110 (1)	0.0339 (7)
C2	0.4075 (1)	-0.0155 (2)	0.4103 (1)	0.0384 (7)
C3	0.4148 (1)	0.0090 (2)	0.3332 (1)	0.0517 (9)
C4	0.3854 (1)	0.1830 (3)	0.2772 (1)	0.0497 (9)
C5	0.4233 (1)	0.3542 (2)	0.3320 (1)	0.0514 (9)
C6	0.4080 (1)	0.4372 (2)	0.3948 (1)	0.0450 (9)
C7	0.4134 (1)	0.3002 (2)	0.4617 (1)	0.0355 (7)
C8	0.3855 (1)	0.3252 (2)	0.5175 (1)	0.0429 (9)
C9	0.3567 (1)	0.1310 (2)	0.4857 (1)	0.0396 (8)
C10	0.2888 (1)	0.0904 (3)	0.4506 (1)	0.0501 (9)
C11	0.2363 (1)	0.1625 (2)	0.3527 (1)	0.0444 (9)
C12	0.2507 (1)	0.1889 (2)	0.2869 (1)	0.0385 (8)
C13	0.3102 (1)	0.1723 (2)	0.3122 (1)	0.0362 (8)
O14	0.3193 (1)	0.1965 (2)	0.2459 (1)	0.0464 (7)
C15	0.4363 (1)	0.3450 (3)	0.6248 (1)	0.0637 (12)
C16	0.3367 (1)	0.4780 (3)	0.4801 (1)	0.0566 (10)
O17	0.4334 (1)	-0.1343 (2)	0.4687 (1)	0.0560 (8)
O18	0.1826 (1)	0.1898 (2)	0.3302 (1)	0.0631 (9)
C19	0.3768 (1)	0.1699 (4)	0.1840 (1)	0.0819 (15)

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.497 (3)	C6—C7	1.506 (3)
C1—C7	1.583 (2)	C7—C8	1.564 (4)
C1—C9	1.537 (4)	C8—C9	1.568 (2)
C1—C13	1.498 (2)	C8—C15	1.527 (2)
C2—C3	1.507 (4)	C8—C16	1.529 (3)
C2—O17	1.208 (2)	C9—C10	1.519 (4)
C3—C4	1.525 (2)	C10—C11	1.512 (2)
C4—C5	1.542 (2)	C11—C12	1.446 (4)
C4—O14	1.469 (4)	C11—O18	1.227 (4)
C4—C19	1.532 (3)	C12—C13	1.343 (4)
C5—C6	1.529 (4)	C13—O14	1.350 (4)
C9—C1—C13	114.2 (2)	C1—C7—C8	88.9 (1)
C7—C1—C13	111.9 (1)	C7—C8—C16	114.0 (1)
C7—C1—C9	88.8 (1)	C7—C8—C15	114.4 (2)
C2—C1—C13	110.9 (1)	C7—C8—C9	88.4 (1)
C2—C1—C9	120.7 (1)	C15—C8—C16	109.4 (2)
C2—C1—C7	107.9 (2)	C9—C8—C16	115.9 (2)
C1—C2—O17	123.5 (2)	C9—C8—C15	113.6 (1)
C1—C2—C3	112.8 (1)	C1—C9—C8	90.4 (1)
C3—C2—O17	123.5 (2)	C8—C9—C10	121.3 (2)
C2—C3—C4	113.7 (2)	C1—C9—C10	116.8 (1)
C3—C4—C19	109.5 (2)	C9—C10—C11	114.8 (2)
C3—C4—O14	108.4 (2)	C10—C11—O18	119.6 (2)
C3—C4—C5	114.5 (1)	C10—C11—C12	118.2 (2)
O14—C4—C19	103.6 (2)	C12—C11—O18	122.1 (2)
C5—C4—C19	110.3 (2)	C11—C12—C13	122.9 (2)
C5—C4—O14	109.9 (2)	C1—C13—C12	124.1 (2)
C4—C5—C6	116.0 (2)	C12—C13—O14	119.1 (2)
C1—C7—C6	111.3 (1)	C1—C13—O14	116.8 (2)
C1—C7—C8	114.4 (1)	C4—O14—C13	117.3 (2)
C6—C7—C8	124.5 (1)		

Data were corrected for Lorentz-polarization and absorption effects. The structure was solved by direct methods. H atoms were obtained from a  $\Delta F$  map and refined isotropically in a separate block. Programs used were SHELXS86 (Sheldrick,

1985), *SHELX76* (Sheldrick, 1976) and *PARST* (Nardelli, 1983). Calculations were performed using a MicroVAX II computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: SZ1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## A Tetralin Derivative

V. KABALEESWARAN,<sup>a</sup> S. S. RAJAN,<sup>a</sup> S. JANARTHANAM<sup>b</sup>  
 AND K. RAJAGOPALAN<sup>b</sup>

<sup>a</sup>Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India, and

<sup>b</sup>Department of Organic Chemistry, University of Madras, Guindy Campus, Madras 600 025, India

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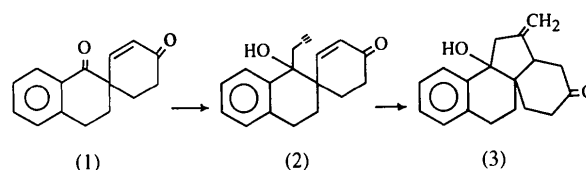
### Abstract

In the structure of 1-hydroxy-1-propynyl-1,2,3,4-tetrahydronaphthalene-2-spiro-(2'-cyclohexen-4'-one), C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>, the C<sub>sp<sup>2</sup></sub> atom at the spiro junction (axial) is *trans* to the propargyl chain (pseudo-axial). The crystal structure is stabilized by O—H...O hydrogen bonds.

### Comment

The structure determination of the title compound, (2), is a continuation of our studies in tin-mediated vinyl

radical cyclization of similarly substituted substrates (Janarthanam, Balakumar & Rajagopalan, 1994). Our efforts were directed towards the synthesis of compound (3) as a model for Retigeranic acid-type molecules (Janarthanam, Shanmugam & Rajagopalan, 1993).



In the scheme above, the stereochemistry at C1 [carbonyl in starting material (1)] is fixed by the fact that the introduction of the three-carbon unit is a stereo-electronically controlled step. During the radical cyclization, *i.e.* (2) → (3), a new stereocenter is generated at atom C4'. As the stereochemistry at C1 is fixed, the extent of stereocontrol obtainable at C4' becomes amenable for study. Thus, the treatment of compound (1) with propargyl sesquialuminium bromide in tetrahydrofuran at 195 K for 3 h gave compound (2) as a mixture of diastereomers in the ratio 90:10. It was of interest to establish the stereochemistry of the major diastereomer with regard to the orientation of the propargyl chain and the enone moiety. The present study reports the X-ray crystallographic investigation of this orientation, as well as the conformation of the partially unsaturated rings.

The central ring adopts a sofa conformation ( $\Delta C_2 = 7.2^\circ$ ) and the enone ring adopts a half-chair conformation ( $\Delta C_5 = 8.2^\circ$ ) (Duax, Weeks & Rohrer, 1976). The bond lengths and angles agree with those of similar systems (Nethaji, 1987; Geetha & Rajan, 1991). The *sp<sup>2</sup>* C4' atom at the spiro junction (axial) is *trans* to the propargyl chain (pseudo-axial).

The molecular packing in the unit cell involves O—H...O4 hydrogen bonding [O1...O4(-x, -y+1, -z+2) 2.905 (2), H...O4 2.06 (3) Å and O1—H...O4 155 (3)°].

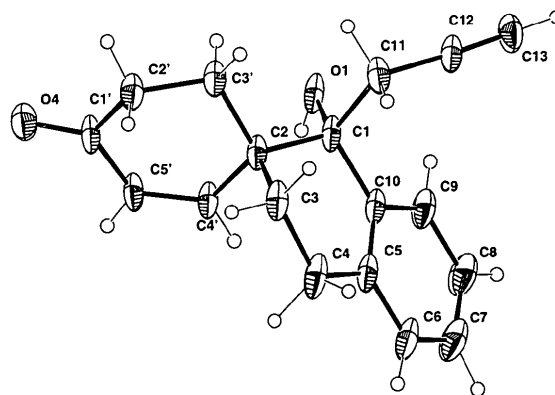


Fig. 1. A perspective diagram of the title compound with ellipsoids plotted at the 30% probability level.