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Structure of a Tetracyclic Intermediate in the Synthesis of *Daphniphyllum* Alkaloids

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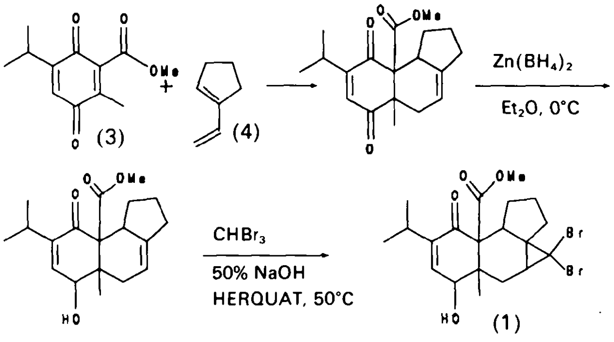
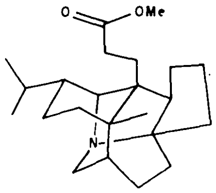
Abstract

Methyl 14,14-dibromo-4-hydroxy-6-isopropyl-3-methyl-7-oxotetracyclo[11.1.0.0^{3,8}.0^{9,13}]tetradec-5-ene-8-carboxylate, $C_{20}H_{26}Br_2O_4$, adopts an overall hemispherical conformation with the three major rings all having *cis* ring fusion and the cyclopropane ring pointing outward from the hemisphere.

Comment

Compound (1) forms part of a many-step sequence of reactions in the projected synthesis of methyl homodaphniphylate (2), a *Daphniphyllum* alkaloid of considerable structural, biological and synthetic interest (Yamamura, 1986). Compound (1) was prepared from thymoquinone-2-carboxylate methyl ester (3) and 1-vinylcyclopentene (4), as shown below. The synthetic complexity involved translates into a compound containing six contiguous asymmetric centres, whose complete structure elucidation can only be obtained by single-crystal X-ray diffraction. Furthermore, this structure determination is also necessary for planning the most appropriate sequence of reactions that will lead to the desired final product (2).





(2)

The hydroxycyclohexenone ring is in a sofa conformation with the methylated ring-junction C atom out of the plane. The fused cyclopropane ring forces the central cyclohexane ring into a half-chair conformation. The cyclopentane ring is in an envelope conformation with C(12) 0.521 (5) Å out of the plane through the other four atoms.

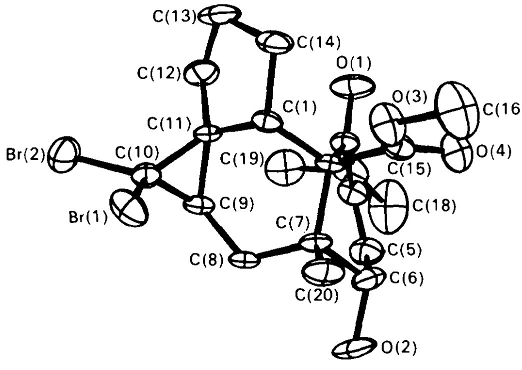


Fig. 1. Projection of $C_{20}H_{26}Br_2O_4$; atoms C(2), C(3) and C(4), which are not labeled, make a six-membered ring with C(5), C(6) and C(7); C(17), also unlabeled and behind this ring, is a substituent at C(4). 50% probability thermal ellipsoids are shown.

Experimental

Crystal data

$C_{20}H_{26}Br_2O_4$
M_r = 490.25
Monoclinic
$P2_1/n$
a = 11.090 (1) Å
b = 8.672 (1) Å
c = 20.699 (2) Å
β = 94.79 (1)°
V = 1983.6 (6) Å^3
Z = 4
D_x = 1.64 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 23 reflections
θ = 17–37°
μ = 5.41 mm^{-1}
T = 292 K
Irregular
0.25 × 0.20 × 0.18 mm
Colourless
Crystal source: from ethyl acetate

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.67, $T_{\max}$ = 1.55
3043 measured reflections
2876 independent reflections
2553 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.061
$\theta_{\max}$ = 60°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 23$
1 standard reflection frequency: 30 min intensity variation: ±1.0%

Refinement

Refinement on F
R = 0.042
wR = 0.049
S = 2.64
2553 reflections
236 parameters
$w = [\sigma^2(|F_o|) + 0.0004|F_o|^2]^{-1}$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.45 e Å^{-3}
$\Delta\rho_{\min}$ = −0.67 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Br(1)	0.7937 (1)	0.1879 (1)	0.4598 (1)	3.40 (2)
Br(2)	0.6047 (1)	0.3497 (1)	0.3613 (1)	4.21 (2)
O(1)	1.0992 (3)	0.5315 (4)	0.2764 (2)	3.7 (1)
O(2)	1.1056 (3)	−0.0893 (4)	0.2880 (2)	4.0 (1)
O(3)	1.2215 (3)	0.3614 (4)	0.4432 (1)	3.5 (1)
O(4)	1.3052 (3)	0.3377 (4)	0.3489 (2)	3.4 (1)
C(1)	0.9944 (3)	0.4001 (5)	0.3901 (2)	1.9 (1)
C(2)	1.0873 (3)	0.3191 (4)	0.3490 (2)	1.7 (1)
C(3)	1.0861 (3)	0.3932 (5)	0.2804 (2)	2.0 (1)
C(4)	1.0778 (4)	0.2966 (5)	0.2219 (2)	2.5 (1)
C(5)	1.1054 (4)	0.1494 (6)	0.2282 (2)	3.0 (2)
C(6)	1.1328 (4)	0.0685 (5)	0.2919 (2)	2.8 (1)
C(7)	1.0604 (3)	0.1397 (5)	0.3449 (2)	2.0 (1)
C(8)	0.9228 (3)	0.1078 (5)	0.3254 (2)	2.3 (1)
C(9)	0.8349 (3)	0.2391 (5)	0.3207 (2)	2.1 (1)
C(10)	0.7707 (3)	0.2901 (5)	0.3783 (2)	2.1 (1)
C(11)	0.8687 (3)	0.3932 (5)	0.3537 (2)	1.8 (1)
C(12)	0.8409 (4)	0.5518 (5)	0.3275 (2)	3.2 (1)
C(13)	0.9011 (5)	0.6578 (6)	0.3789 (3)	4.8 (2)
C(14)	1.0146 (4)	0.5722 (5)	0.4059 (2)	3.0 (1)
C(15)	1.2163 (4)	0.3408 (5)	0.3790 (2)	2.3 (1)
C(16)	1.3419 (5)	0.3719 (9)	0.4766 (3)	5.4 (2)
C(17)	1.0460 (4)	0.3770 (6)	0.1583 (2)	3.5 (2)
C(18)	1.1024 (6)	0.299 (1)	0.1017 (3)	6.8 (3)
C(19)	0.9106 (5)	0.3916 (7)	0.1445 (3)	4.6 (2)
C(20)	1.1009 (4)	0.0575 (5)	0.4091 (2)	3.3 (1)

Table 2. *Geometric parameters* (Å, °)

Br(1)—C(10)	1.904 (4)	Br(2)—C(10)	1.916 (4)
O(1)—C(3)	1.212 (5)	O(2)—C(6)	1.402 (5)
O(3)—C(15)	1.337 (5)	O(3)—C(16)	1.454 (6)
O(4)—C(15)	1.210 (5)	C(1)—C(2)	1.557 (5)
C(1)—C(11)	1.529 (5)	C(1)—C(14)	1.540 (6)
C(2)—C(3)	1.558 (5)	C(2)—C(7)	1.585 (6)
C(2)—C(15)	1.523 (6)	C(3)—C(4)	1.469 (6)
C(4)—C(5)	1.317 (7)	C(4)—C(17)	1.505 (6)
C(5)—C(6)	1.502 (6)	C(6)—C(7)	1.542 (6)
C(7)—C(8)	1.570 (6)	C(7)—C(20)	1.541 (6)
C(8)—C(9)	1.497 (6)	C(9)—C(10)	1.505 (5)
C(9)—C(11)	1.533 (6)	C(10)—C(11)	1.527 (5)
C(11)—C(12)	1.501 (6)	C(12)—C(13)	1.518 (8)
C(13)—C(14)	1.527 (7)	C(17)—C(18)	1.531 (8)
C(17)—C(19)	1.510 (7)		
C(15)—O(3)—C(16)	116.3 (4)	C(2)—C(1)—C(11)	109.3 (3)
C(2)—C(1)—C(14)	117.5 (3)	C(11)—C(1)—C(14)	104.7 (3)
C(1)—C(2)—C(3)	110.9 (3)	C(1)—C(2)—C(7)	110.0 (3)
C(1)—C(2)—C(15)	111.3 (3)	C(3)—C(2)—C(7)	111.6 (3)
C(3)—C(2)—C(15)	104.9 (3)	C(7)—C(2)—C(15)	108.0 (3)
O(1)—C(3)—C(2)	118.6 (4)	O(1)—C(3)—C(4)	120.5 (4)
C(2)—C(3)—C(4)	120.8 (3)	C(3)—C(4)—C(5)	118.2 (4)
C(3)—C(4)—C(17)	116.8 (4)	C(5)—C(4)—C(17)	124.8 (4)
C(4)—C(5)—C(6)	124.6 (4)	O(2)—C(6)—C(5)	112.2 (4)
O(2)—C(6)—C(7)	108.0 (3)	C(5)—C(6)—C(7)	111.0 (4)
C(2)—C(7)—C(6)	108.9 (3)	C(2)—C(7)—C(8)	111.2 (3)
C(2)—C(7)—C(20)	111.6 (3)	C(6)—C(7)—C(8)	107.4 (3)
C(6)—C(7)—C(20)	107.3 (3)	C(8)—C(7)—C(20)	110.3 (3)
C(7)—C(8)—C(9)	119.8 (3)	C(8)—C(9)—C(10)	121.4 (3)
C(8)—C(9)—C(11)	120.0 (3)	C(10)—C(9)—C(11)	60.3 (3)
Br(1)—C(10)—Br(2)	110.1 (2)	Br(1)—C(10)—C(9)	121.9 (3)
Br(1)—C(10)—C(11)	121.4 (3)	Br(2)—C(10)—C(9)	116.4 (3)
Br(2)—C(10)—C(11)	118.7 (3)	C(9)—C(10)—C(11)	60.7 (3)
C(1)—C(11)—C(9)	115.6 (3)	C(1)—C(11)—C(10)	120.2 (3)
C(1)—C(11)—C(12)	107.1 (3)	C(9)—C(11)—C(10)	58.9 (2)
C(9)—C(11)—C(12)	127.1 (3)	C(10)—C(11)—C(12)	121.8 (3)
C(11)—C(12)—C(13)	103.7 (4)	C(12)—C(13)—C(14)	105.3 (4)
C(1)—C(14)—C(13)	107.0 (4)	O(3)—C(15)—O(4)	123.0 (4)
O(3)—C(15)—C(2)	112.5 (3)	O(4)—C(15)—C(2)	124.4 (4)
C(4)—C(17)—C(18)	112.6 (4)	C(4)—C(17)—C(19)	111.2 (4)
C(18)—C(17)—C(19)	110.8 (5)		

Data were corrected for Lp and absorption effects. The structure was solved by direct methods. H atoms were found by difference synthesis and included as fixed contributors with an overall isotropic temperature factor that refined to $U_{\rm iso}$ = 0.064 (3) Å^2. Programs used were: *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). The refinement was by block-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71425 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1055]

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Structure of 4-Chlorochalcone

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Abstract

The title compound, 3-(4-chlorophenyl)-1-phenyl-2-propen-1-one, $C_{15}H_{11}ClO$, has a torsion angle of 7.1° for O(1)—C(9)—C(8)—C(7) of the 2-propen-1-one moiety. H atoms in the central propenone group are *trans* and the dihedral angle between the phenyl rings is 14.34°.

Comment

The final atomic coordinates and thermal parameters are given in Table 1, bond lengths and angles are listed in Table 2 and several least-squares planes are given in Table 3. The molecular configuration and the packing of molecules in unit cell are shown in Figs. 1 and 2, respectively.

The torsion angle for O(1)—C(9)—C(8)—C(7) of the C_2H_2CO group is 7.1°. The H atoms are *trans* in the —C=C— part. The dihedral angles between phenyl rings and O(1)—C(9)—C(8)—C(7) are 14.3, 16.3 and 12.3°, respectively. It is significant that conjugation in the title compound is better than in 4-bromochalcone (Li, Pa & Su, 1992).

The chalcone derivatives are newly developed organic crystals with nonlinear optical coefficients (Fichou, Watanabe, Takeda, Miyata, Goto & Nakayama, 1988). In order to explore the relationship between their structure and nonlinear optical properties, we synthesized a series of substituted chalcones. The title compound is one of them, which happens to crystallize in a centrosymmetric space group and therefore has no nonlinear optical properties. This has been confirmed by second harmonic generation (SHG) efficiency measurements on a powder sample using the method of Kurtz & Perry (1968).

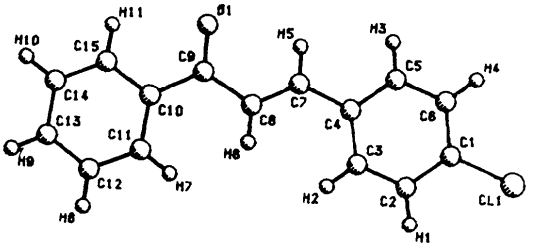

Fig. 1. The molecular structure of the title compound.

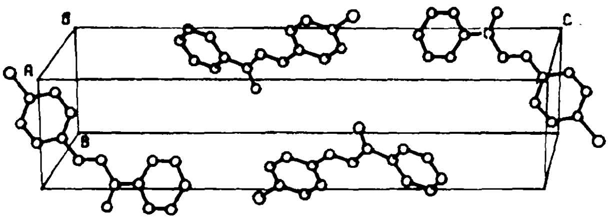

Fig. 2. The packing of the title compound in the unit cell.

Experimental

Crystal data

$C_{15}H_{11}ClO$
M_r = 242.70
Monoclinic
$P2_1/c$
a = 8.211 (2) Å
b = 5.869 (2) Å
c = 25.291 (5) Å
β = 99.18°
V = 1203.1 (5) Å^3
Z = 4

D_x = 1.340 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 6.5- 11°
μ = 0.293 mm^{-1}
T = 294 K
Plate
1.0 × 0.5 × 0.1 mm
Colourless

Data collection

Rigaku MSC/AFC-5*R* diffractometer
ω-2θ scans
Absorption correction: empirical based on ψ scans (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.737, $T_{\max}$ = 1.341
2498 measured reflections
2328 independent reflections

1264 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max}$ = 25°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 7$
$l = -30 \rightarrow 30$
3 standard reflections monitored every 250 reflections intensity variation: 0.1%

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