Table 4. *Selected geometric parameters* (Å, °) *for* (II)

C1—C2	1.375 (4)	C16—C17	1.517 (3)
C1—C6	1.406 (3)	C17—O18	1.301 (3)
C10—C9	1.542 (3)	C17—O19	1.188 (3)
C10—C11	1.492 (3)	C2—C3	1.381 (4)
C10—C16	1.554 (3)	C3—C4	1.374 (4)
C11—N7	1.383 (3)	C4—C5	1.394 (3)
C11—O12	1.244 (3)	C5—C6	1.393 (3)
C13—C9	1.510 (3)	C6—N7	1.399 (3)
C13—C14	1.314 (4)	C8—N7	1.486 (3)
C14—C15	1.505 (3)	C8—C9	1.472 (3)
C15—C16	1.565 (3)	C9—O20	1.453 (3)
C15—O20	1.450 (3)		
C11—C10—C9	102.4 (3)	C2—C3—C4	119.7 (6)
C11—C10—C16	120.9 (4)	C3—C4—C5	120.7 (5)
C16—C10—C9	102.5 (3)	C4—C5—C6	119.8 (4)
C10—C11—N7	108.9 (4)	C1—C6—C5	118.8 (4)
C10—C11—O12	128.3 (4)	C1—C6—N7	119.0 (4)
N7—C11—O12	122.7 (4)	C5—C6—N7	122.2 (4)
C14—C13—C9	106.9 (5)	C9—C8—N7	103.4 (4)
C13—C14—C15	105.9 (5)	C10—C9—C8	105.7 (4)
C14—C15—C16	106.6 (4)	C10—C9—C13	109.9 (4)
C14—C15—O20	101.2 (4)	C10—C9—O20	98.8 (3)
C16—C15—O20	100.8 (3)	C13—C9—C8	127.9 (4)
C10—C16—C15	100.1 (3)	C13—C9—O20	99.7 (3)
C10—C16—C17	115.5 (4)	C8—C9—O20	111.3 (4)
C15—C16—C17	113.1 (4)	C11—N7—C6	127.3 (4)
C16—C17—O18	111.4 (4)	C11—N7—C8	111.1 (4)
C16—C17—O19	125.3 (4)	C6—N7—C8	121.6 (4)
O18—C17—O19	123.4 (4)	C15—O20—C9	96.5 (4)
C1—C2—C3	120.7 (6)		

For both compounds, data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: local program (CRMC2, France); program(s) used to solve structures: *MULTAN*80 (Main *et al.*, 1980); program(s) used to refine structures: *SHELX*76 (Sheldrick, 1976); molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Bioactive β-Dihydroagarofuran Sesquiterpenoid

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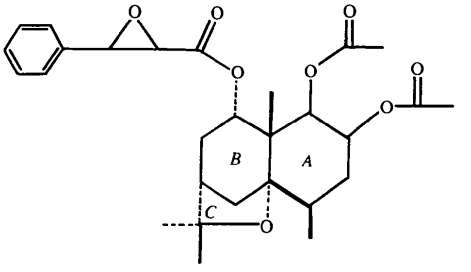
Abstract

The structure of a new sesquiterpene, 1β,2β-diacetoxy-9α-(3-phenyl-2-oxiranylcarboxy)-β-dihydroagarofuran, from *Celastraceae* has been determined and found to have a very interesting three-membered ring.

Comment

Historically, bioactive β-dihydroagarofuran sesquiterpenoids of the plant genus *Celastraceae* have been used as insecticides in China. Recently, a new sesquiterpene, 1β,2β-diacetoxy-9α-(3-phenyl-2-oxiranylcarboxy)-β-dihydroagarofuran, (I), has been isolated from the seeds of *C. gemmatus loes*. Experiments show that for the cabbage worm, *Pieris rapae* (a main species of injurous insects), the death rate is about 50% at a concentration of 500 p.p.m.



(I)

Fig. 1 shows the structure of the β-dihydroagarofuran sesquiterpenoid. Both rings *A* and *B* adopt the chair conformation and they are almost parallel. The *C* ring is virtually perpendicular to *A* and *B*. The mean dihedral angle between the *C* and *A*/*B* rings is 83°. The 9α-hydroxy group of the *B* ring is esterified by an epoxidized cinnamoyl residue. The presence of the epoxy group is difficult to distinguish by chemical means or magnetic resonance, because it is easily converted into cinnamic acid in aqueous solution.

Related studies on dihydroagarofuran sesquiterpenoids have been reported by Delle Monache, Marini Bettolo & Bernays (1984), Jacobson (1958), Yamada, Shizuri & Hirate (1978), Wakabayashi *et al.* (1988) and Rosza, Perjesi, Pelzer, Argay & Kálmán (1989).

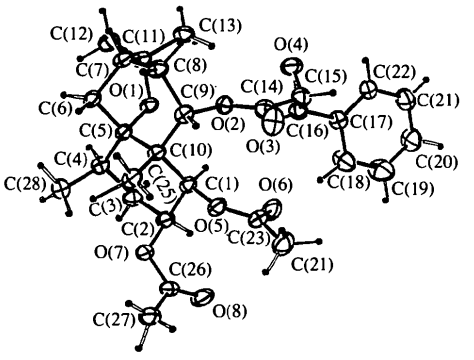


Fig. 1. The labelled molecular model of β-dihydroagarofuran sesquiterpenoid.

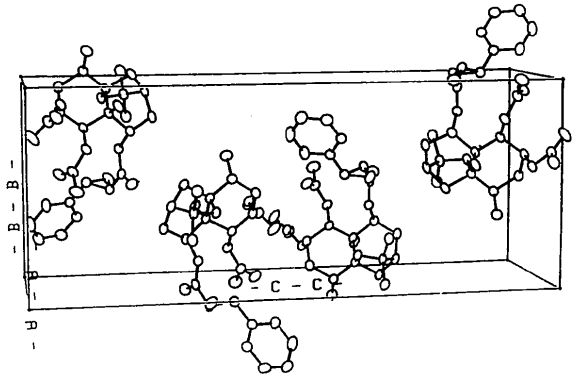


Fig 2. Packing in the unit cell.

Experimental

Crystal data

$C_{28}H_{36}O_8$
M_r = 500.59
Orthorhombic
$P2_12_12_1$
a = 8.976 (1) Å
b = 10.800 (1) Å
c = 27.401 (3) Å
V = 2656.3 (5) Å^3
Z = 4
D_x = 1.252 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.0851 mm^{-1}
T = 293 K
Tabular
0.5 × 0.3 × 0.3 mm
Colourless, transparent
Crystal source: recrystallized from methanol

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: 7 sample points
T_{min} = 0.96, T_{max} = 0.99
2911 independent reflections
2330 observed reflections [$I \geq 3.0\sigma(I)$]

R_{int} = 0.03
θ_{max} = 25°
h = 0 → 10
k = 0 → 12
l = 0 → 32
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F
R = 0.037
wR = 0.035
S = 0.241
2330 reflections
470 parameters
All H-atom parameters refined

Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.76
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O(1)	0.1586 (2)	0.3984 (2)	0.34710 (7)	3.51 (4)
O(2)	0.2661 (2)	0.1571 (2)	0.31703 (7)	3.67 (4)
O(3)	0.4194 (3)	−0.0002 (2)	0.29687 (9)	6.36 (6)
O(4)	0.0369 (3)	−0.0084 (3)	0.33162 (9)	6.34 (6)
O(5)	0.5317 (2)	0.1805 (2)	0.38517 (8)	4.06 (5)
O(6)	0.4029 (3)	0.0532 (2)	0.43444 (9)	5.70 (6)
O(7)	0.6009 (2)	0.3981 (2)	0.43242 (8)	4.41 (5)
O(8)	0.6641 (3)	0.2494 (3)	0.48596 (9)	7.04 (7)
C(1)	0.4174 (3)	0.2754 (3)	0.3883 (1)	3.38 (6)
C(2)	0.4463 (4)	0.3562 (3)	0.4326 (1)	3.96 (7)
C(3)	0.3400 (4)	0.4664 (3)	0.4330 (1)	4.49 (7)
C(4)	0.3281 (4)	0.5394 (3)	0.3853 (1)	4.21 (7)
C(5)	0.3064 (3)	0.4530 (3)	0.3416 (1)	3.44 (6)
C(6)	0.2996 (4)	0.5197 (3)	0.2919 (1)	4.11 (7)
C(7)	0.2006 (4)	0.4294 (3)	0.2643 (1)	4.14 (7)
C(8)	0.2934 (4)	0.3130 (3)	0.2531 (1)	4.17 (7)
C(9)	0.3686 (3)	0.2509 (3)	0.2977 (1)	3.72 (7)
C(10)	0.4172 (3)	0.3420 (3)	0.3384 (1)	3.38 (6)
C(11)	0.0760 (4)	0.4101 (3)	0.3014 (1)	4.00 (7)
C(12)	−0.0285 (4)	0.5217 (4)	0.3045 (1)	5.09 (8)
C(13)	−0.0203 (4)	0.2948 (4)	0.2948 (1)	4.69 (8)
C(14)	0.3049 (4)	0.0388 (3)	0.3131 (1)	4.33 (7)
C(15)	0.1877 (4)	−0.0467 (3)	0.3331 (1)	4.69 (8)
C(16)	0.1065 (4)	−0.0175 (3)	0.3782 (1)	4.16 (7)
C(17)	0.0555 (4)	−0.1201 (3)	0.4103 (1)	4.12 (7)
C(18)	0.1126 (5)	−0.1267 (4)	0.4571 (1)	6.3 (1)
C(19)	0.0713 (6)	−0.2233 (5)	0.4870 (1)	7.9 (1)
C(20)	−0.0276 (5)	−0.3109 (4)	0.4717 (1)	6.6 (1)
C(21)	−0.0884 (5)	−0.3015 (4)	0.4262 (2)	6.3 (1)
C(22)	−0.0462 (4)	−0.2061 (3)	0.3953 (1)	5.03 (8)
C(23)	0.5127 (4)	0.0764 (3)	0.4110 (1)	4.77 (8)
C(24)	0.6439 (5)	−0.0072 (4)	0.4061 (2)	7.3 (1)
C(25)	0.5767 (4)	0.3846 (3)	0.3239 (1)	4.56 (7)
C(26)	0.6995 (4)	0.3275 (3)	0.4575 (1)	4.78 (8)
C(27)	0.8555 (4)	0.3575 (4)	0.4446 (1)	5.87 (9)
C(28)	0.4500 (5)	0.6384 (4)	0.3801 (1)	5.91 (9)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(5)	1.459 (4)	C(5)—C(10)	1.560 (4)
O(1)—C(11)	1.461 (4)	C(6)—C(7)	1.521 (5)
O(2)—C(9)	1.467 (4)	C(7)—C(8)	1.539 (5)
O(2)—C(14)	1.328 (5)	C(7)—C(11)	1.526 (4)
O(3)—C(14)	1.197 (4)	C(8)—C(9)	1.549 (4)
O(4)—C(15)	1.416 (5)	C(9)—C(10)	1.550 (4)
O(4)—C(16)	1.424 (4)	C(10)—C(25)	1.555 (4)
O(5)—C(1)	1.453 (4)	C(11)—C(12)	1.529 (6)
O(5)—C(23)	1.339 (5)	C(11)—C(13)	1.526 (5)
O(6)—C(23)	1.202 (4)	C(14)—C(15)	1.503 (6)
O(7)—C(2)	1.460 (4)	C(15)—C(16)	1.468 (5)
O(7)—C(26)	1.355 (4)	C(16)—C(17)	1.488 (5)
O(8)—C(26)	1.192 (5)	C(17)—C(18)	1.383 (5)
C(1)—C(2)	1.518 (4)	C(17)—C(22)	1.367 (5)
C(1)—C(10)	1.544 (4)	C(18)—C(19)	1.378 (6)
C(2)—C(3)	1.525 (5)	C(19)—C(20)	1.363 (7)
C(3)—C(4)	1.531 (5)	C(20)—C(21)	1.364 (6)
C(4)—C(5)	1.531 (4)	C(21)—C(22)	1.387 (5)
C(4)—C(28)	1.537 (5)	C(23)—C(24)	1.491 (6)
C(5)—C(6)	1.542 (4)	C(26)—C(27)	1.480 (5)

C(5)—O(1)—C(11)	109.9 (3)	C(5)—C(10)—C(9)	110.4 (2)
C(9)—O(2)—C(14)	118.1 (2)	C(5)—C(10)—C(25)	111.9 (3)
C(15)—O(4)—C(16)	62.3 (2)	C(9)—C(10)—C(25)	105.2 (2)
C(1)—O(5)—C(23)	118.1 (2)	O(1)—C(11)—C(7)	102.2 (2)
C(2)—O(7)—C(26)	116.4 (2)	O(1)—C(11)—C(12)	109.3 (3)
O(5)—C(1)—C(2)	109.4 (2)	O(1)—C(11)—C(13)	108.6 (3)
O(5)—C(1)—C(10)	106.1 (2)	C(7)—C(11)—C(12)	112.3 (3)
C(2)—C(1)—C(10)	116.1 (3)	C(7)—C(11)—C(13)	116.6 (3)
O(7)—C(2)—C(1)	109.8 (2)	C(12)—C(11)—C(13)	107.6 (3)
O(7)—C(2)—C(3)	110.7 (3)	O(2)—C(14)—O(3)	126.4 (3)
C(1)—C(2)—C(3)	110.4 (3)	O(2)—C(14)—C(15)	112.2 (3)
C(2)—C(3)—C(4)	116.1 (3)	O(3)—C(14)—C(15)	121.3 (3)
C(3)—C(4)—C(5)	111.3 (3)	O(4)—C(15)—C(14)	118.6 (3)
C(3)—C(4)—C(28)	112.8 (3)	O(4)—C(15)—C(16)	59.1 (2)
C(5)—C(4)—C(28)	116.4 (3)	C(14)—C(15)—C(16)	121.4 (3)
O(1)—C(5)—C(4)	106.4 (2)	O(4)—C(16)—C(15)	58.6 (2)
O(1)—C(5)—C(6)	104.1 (2)	O(4)—C(16)—C(17)	116.6 (3)
O(1)—C(5)—C(10)	106.0 (2)	C(15)—C(16)—C(17)	119.4 (3)
C(4)—C(5)—C(6)	114.3 (3)	C(16)—C(17)—C(18)	118.3 (3)
C(4)—C(5)—C(10)	115.6 (2)	C(16)—C(17)—C(22)	122.2 (3)
C(6)—C(5)—C(10)	109.5 (2)	C(18)—C(17)—C(22)	119.5 (3)
C(5)—C(6)—C(7)	99.4 (3)	C(17)—C(18)—C(19)	119.4 (4)
C(6)—C(7)—C(8)	107.8 (3)	C(18)—C(19)—C(20)	121.2 (4)
C(6)—C(7)—C11)	100.6 (2)	C(19)—C(20)—C(21)	119.4 (4)
C(8)—C(7)—C(11)	114.7 (3)	C(20)—C(21)—C(22)	120.3 (4)
C(7)—C(8)—C(9)	115.7 (3)	C(17)—C(22)—C(21)	120.2 (3)
O(2)—C(9)—C(8)	108.1 (2)	O(5)—C(23)—O(6)	124.2 (3)
O(2)—C(9)—C(10)	110.7 (2)	O(5)—C(23)—C(24)	111.1 (4)
C(8)—C(9)—C(10)	114.6 (3)	O(6)—C(23)—C(24)	124.7 (3)
C(1)—C(10)—C(5)	108.0 (2)	O(7)—C(26)—O(8)	123.8 (3)
C(1)—C(10)—C(9)	110.0 (3)	O(7)—C(26)—C(27)	111.9 (3)
C(1)—C(10)—C(25)	111.3 (2)	O(8)—C(26)—C(27)	124.4 (3)

Intensities were measured with a scan width of $(0.55 + 0.35\tan\theta)°$ and a scan rate of 1.0–8.24° min^{-1}, extended 25% on each side for background measurement. $\sigma^2(I)$ was calculated as $S + 4(B_1 + B_2) + (0.04S)^2$, where S = scan, B_1 and B_2 = background counts. The structure was solved by direct methods using the program *RANTAN* (Yao, 1981) and refined by block and full-matrix least-squares calculations on F. Anisotropic displacement parameters were refined for non-H atoms. All H atoms were located from difference maps, included in the structure-factor calculations and refined with fixed isotropic temperature factors (5.0 $Å^2$). All calculations were performed on a PDP 11/44 computer with the Enraf–Nonius CAD-4 *SDP* package (Enraf–Nonius, 1985).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71272 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0163]

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Ethylenediamine-*N*,*N*′-dimethyl-*N*,*N*′-2,2′-di-6-*tert*-butyl-1,4-benzoquinone

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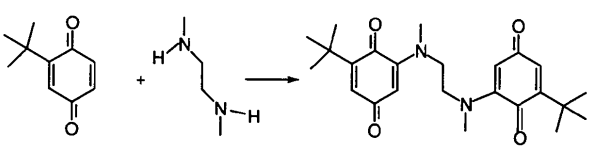
Abstract

The title molecule, $C_{24}H_{32}N_2O_4$, is crystallographically centrosymmetric with the two benzoquinone rings parallel. Benzoquinone rings generally have a flattened envelope conformation with localized double bonds. The presence of two substituents on one side of the benzoquinone ring leads to an unsymmetrical degree of π-electron delocalization which is most significant along N1—C1=C2—C3. The *tert*-butyl groups are *anti* to the methyl groups which enables an effective three-dimensional packing of the molecules. The molecular structure is dominated by van der Waals interactions and an intermolecular hydrogen bond [O1···H4*a* = 2.46 Å].

Comment

As a part of our ongoing studies of the coupling reactions between amines and various quinones, we have prepared the title compound, (I), by the reaction of *tert*-butylbenzoquinone with *N*,*N*′-dimethylethylenediamine. To our knowledge, this is the first example of a 2:1 quinone–amine adduct characterized crystallographically. There are few structures of quinone–amine adducts reported in the literature; all have only one quinone moiety in the molecule and either two (Schmalle, Bürgi & Rüedi, 1991; Retting & Trotter, 1975; Kulpe, 1970) or four (Bock, Ruppert, Nather & Havlas, 1991) amine substituents. The X-ray analysis confirms the quinoid structure of the product and the regioselectivity of the reaction. The full account of spectroscopic and kinetic data will be published elsewhere (Raptova & Horak, 1995).



(I)