

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (\AA^2)
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	-0.3106 (3)	-0.2543 (2)	0.0643 (2)	0.0326 (6)
C2	-0.1935 (3)	-0.2699 (2)	0.1337 (2)	0.0337 (6)
C3	-0.1846 (3)	-0.2002 (3)	0.1874 (2)	0.0431 (7)
C4	-0.0852 (3)	-0.2190 (3)	0.2567 (3)	0.0521 (9)
C5	0.0079 (3)	-0.3072 (3)	0.2754 (3)	0.0577 (10)
C6	0.0014 (3)	-0.3776 (3)	0.2244 (3)	0.0533 (9)
C7	-0.0984 (3)	-0.3604 (3)	0.1549 (2)	0.0445 (8)
C8	-0.4154 (3)	-0.3173 (2)	0.1507 (2)	0.0319 (6)
C9	-0.3991 (3)	-0.4406 (2)	0.2185 (2)	0.0377 (7)
C10	-0.4870 (3)	-0.5027 (3)	0.2990 (2)	0.0426 (8)
C11	-0.5950 (3)	-0.4434 (3)	0.3150 (2)	0.0462 (8)
C12	-0.6134 (3)	-0.3220 (3)	0.2506 (2)	0.0449 (8)
C13	-0.5242 (3)	-0.2601 (3)	0.1699 (2)	0.0383 (7)
C14	-0.2884 (3)	-0.3081 (2)	-0.0158 (2)	0.0339 (7)
C15	-0.3860 (3)	-0.3611 (2)	-0.0386 (2)	0.0405 (7)
C16	-0.3696 (4)	-0.4037 (3)	-0.1157 (3)	0.0494 (8)
C17	-0.2562 (4)	-0.3959 (3)	-0.1702 (3)	0.0544 (9)
C18	-0.1588 (4)	-0.3416 (3)	-0.1519 (3)	0.0518 (8)
C19	-0.1752 (3)	-0.2964 (3)	-0.0762 (2)	0.0422 (7)
C20	-0.3479 (3)	-0.1162 (2)	-0.0110 (2)	0.0337 (7)
C21	-0.4568 (3)	-0.0985 (2)	-0.0847 (2)	0.0342 (7)
C22	-0.4565 (3)	-0.0273 (2)	-0.1934 (2)	0.0355 (7)
C23	-0.3471 (2)	0.0400 (2)	-0.2536 (2)	0.0331 (6)
C24	-0.2385 (3)	0.0222 (2)	-0.1855 (2)	0.0348 (7)
C25	-0.2381 (3)	-0.0475 (2)	-0.0764 (2)	0.0362 (7)
C26	-0.3477 (3)	0.1151 (2)	-0.3653 (2)	0.0348 (7)
C27	-0.4634 (3)	0.1464 (2)	-0.4329 (2)	0.0359 (7)
C28	-0.5763 (3)	0.1903 (3)	-0.4052 (3)	0.0478 (8)
C29	-0.6818 (3)	0.2200 (3)	-0.4704 (3)	0.0585 (10)
C30	-0.6758 (3)	0.2055 (3)	-0.5652 (3)	0.0545 (9)
C31	-0.5639 (3)	0.1658 (3)	-0.5959 (3)	0.0477 (8)
C32	-0.4585 (3)	0.1368 (3)	-0.5303 (2)	0.0415 (7)
C33	-0.2325 (3)	0.1731 (2)	-0.4282 (2)	0.0357 (7)
C34	-0.2375 (3)	0.2970 (3)	-0.4935 (2)	0.0410 (7)
C35	-0.1335 (3)	0.3534 (3)	-0.5561 (2)	0.0496 (8)
C36	-0.0240 (3)	0.2880 (3)	-0.5570 (3)	0.0534 (9)
C37	-0.0170 (3)	0.1647 (3)	-0.4944 (3)	0.0541 (9)
C38	-0.1209 (3)	0.1082 (3)	-0.4302 (2)	0.0445 (8)
C15	-0.1602 (8)	0.1440 (8)	0.2444 (8)	0.149 (3)
C25	-0.1369 (9)	0.1050 (6)	0.1644 (15)	0.180 (6)
C35	-0.1713 (6)	0.1783 (6)	0.0572 (8)	0.112 (2)
C45	-0.2240 (5)	0.2821 (5)	0.0336 (4)	0.0844 (13)
C55	-0.2451 (6)	0.3185 (5)	0.1108 (4)	0.101 (2)
C65	-0.2134 (6)	0.2488 (6)	0.2170 (5)	0.107 (2)

Table 2. *Selected geometric parameters* (\AA , $^\circ$)

C1—C14	1.537 (4)	C22—C23	1.463 (4)
C1—C2	1.543 (4)	C23—C26	1.376 (4)
C1—C8	1.544 (4)	C23—C24	1.453 (4)
C1—C20	1.597 (4)	C24—C25	1.337 (4)
C20—C25	1.493 (4)	C26—C33	1.483 (4)
C20—C21	1.503 (4)	C26—C27	1.485 (4)
C21—C22	1.335 (4)		
C14—C1—C2	113.4 (2)	C21—C22—C23	122.8 (3)
C14—C1—C8	111.1 (2)	C26—C23—C24	122.8 (2)
C2—C1—C8	104.2 (2)	C26—C23—C22	122.8 (2)
C14—C1—C20	105.6 (2)	C24—C23—C22	114.4 (2)
C2—C1—C20	110.5 (2)	C25—C24—C23	123.5 (3)
C8—C1—C20	112.1 (2)	C24—C25—C20	124.1 (3)
C25—C20—C21	110.9 (2)	C23—C26—C33	122.6 (2)
C25—C20—C1	113.1 (2)	C23—C26—C27	123.2 (2)
C21—C20—C1	111.6 (2)	C33—C26—C27	114.3 (2)
C22—C21—C20	124.3 (3)		

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Microbial Transformation of a Dihydroxybiphenyl

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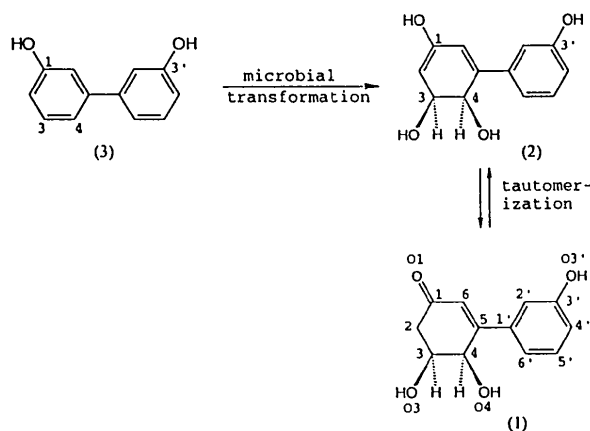
Abstract

The X-ray crystal structure of (3*S*,4*R*)-3,4-dihydroxy-5-(3-hydroxyphenyl)-5-cyclohexen-1-one, C₁₂H₁₂O₄, was determined and showed that the molecule consists of

a conjugated cyclohexenone ring substituted by two hydroxyl groups and a 3-hydroxyphenyl group. There are three O—H...O intermolecular hydrogen bonds.

Comment

The title compound, (1), was obtained as the major transformation product from 1,3'-biphenyldiol† (3) using *Pseudomonas testosteroni* strain B-356. Enzymatic dihydroxylation of (3) at the 3- and 4-positions initially produces (3*S*,4*R*)-3,4-dihydro-biphenyl-1,3,4,3'-tetraol (2) via the biphenyl pathway (Sondossi, Sylvestre, Bariault & Ahmad, 1994). Structure (2) presumably tautomerizes to compound (1) which is not degraded further by strain B-356 and accumulates in the medium. The organism, cultivation conditions, preparation of resting bacterial suspensions and metabolite extraction have been described previously (Sondossi, Sylvestre & Ahmad, 1992). Compound (1) was extracted from a suspension with ethyl acetate at neutral pH. Gas chromatographic analysis of the extract showed that it contained compound (1) at $\geq 99\%$ purity. The organic phase was evaporated under a stream of nitrogen. The 3,4,3'-tris(trimethylsiloxy) derivative of (1) was analyzed by mass spectroscopy [prominent peaks are: m/z 436 (M^+), 421 ($M-15$) and 320 (intense, $M-116$)].



Compound (1) was dissolved in a minimum amount of ethyl acetate. This solution was placed in a stoppered tube at 277 K for two weeks, during which time small crystals formed. The liquid phase was poured off. The crystals were washed twice with cold ether and then transferred to a glass microscope slide for crystallographic analysis. An *ORTEP* drawing (Johnson, 1965) of (1) is shown in Fig. 1 and a unit-cell packing diagram is shown in Fig. 2.

There are three contacts involving oxygen that are consistent with intermolecular hydrogen bonding: O4...O3ⁱ, O3...O1ⁱⁱ and O3'...O4ⁱⁱⁱ of 2.821 (3),

† Non-standard numbering of atoms is used in structures (2) and (3) to facilitate comparison with structure (1) (see reaction scheme).

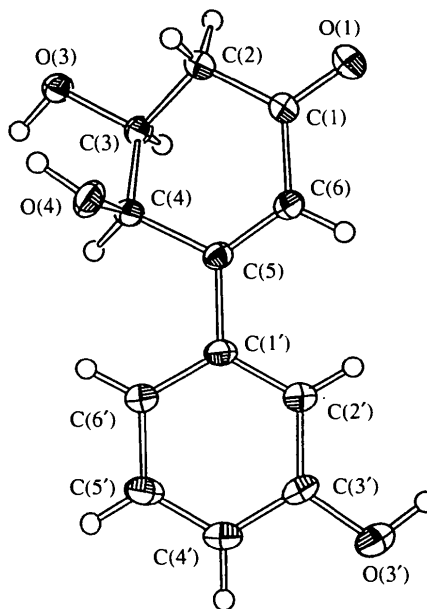


Fig. 1. *ORTEP* view (Johnson, 1965) of (1) with displacement ellipsoids drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

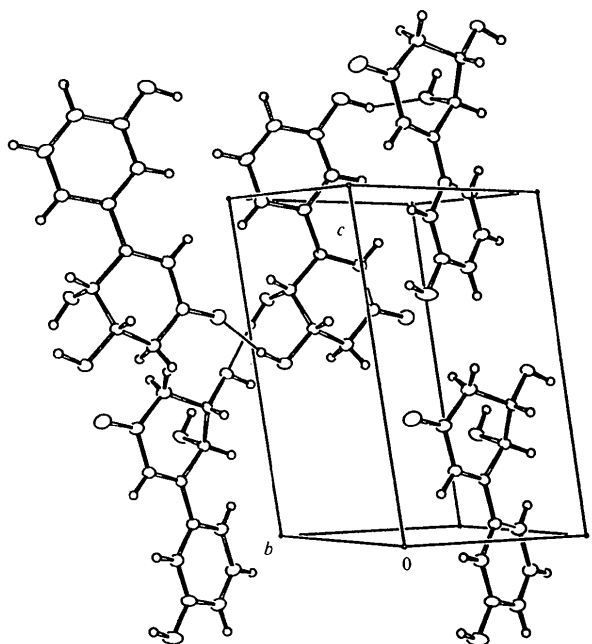


Fig. 2. Unit-cell packing diagram of (1) showing intermolecular hydrogen bonds as thin lines.

2.810 (3) and 2.700 (4) Å, respectively, which are near the sum of the van der Waals radii (2.8 Å; Bondi, 1964) [symmetry codes: (i) $-x, \frac{1}{2} + y, 1 - z$; (ii) $x - 1, y, z$; (iii) $1 - x, y - \frac{1}{2}, 2 - z$]. The angles O4—HO4...O3ⁱ, O3—HO3...O1ⁱⁱ and O3'—HO3'...O4ⁱⁱⁱ [143 (3), 167 (3) and 151 (5)°, respectively] are also consistent with intermolecular hydrogen bonding.

As expected, atoms C1', C2', C3', C4', C5' and C6' are nearly coplanar. However, the least-squares plane defined by atoms C4, C5, C6 and C1 intersects the aromatic ring plane at an angle of 7.71 (17)°. Non-coplanarity of the second plane with the first may be a consequence of the enone ring assuming a conformation in the crystal lattice that optimizes hydrogen-bonding interactions.

Experimental

Crystal data

C₁₂H₁₂O₄
M_r = 220.23
 Monoclinic
*P*2₁
a = 6.929 (3) Å
b = 6.725 (3) Å
c = 10.778 (5) Å
 β = 99.27 (4)°
V = 495.7 (4) Å³
Z = 2
D_x = 1.476 Mg m⁻³

Cu K α radiation
 λ = 1.5418 Å
 Cell parameters from 25 reflections
 θ = 20–25°
 μ = 0.88 mm⁻¹
T = 235 K
 Plate
 0.35 {1 $\bar{1}$ 0} × 0.34 {110} × 0.016 {001} mm
 Transparent and colourless

Data collection

Enraf–Nonius diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3726 measured reflections
 1885 independent reflections
 1769 observed reflections
 [*I* > 1.96 σ (*I*)]

*R*_{int} = 0.055
 θ_{\max} = 70°
h = -8 → 8
k = 0 → 8
l = 0 → 13
 3 standard reflections
 frequency: 60 min
 intensity decay: <1.4%

Refinement

Refinement on *F*
R = 0.046
 wR = 0.053
S = 2.84
 954 reflections
 146 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$
 $(\Delta/\sigma)_{\max} = 0.17$

$\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: 0.07 (2) (secondary)
 Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O1	0.6945 (3)	-0.2564	0.6488 (2)	3.52 (14)
O3	0.0095 (3)	-0.2471 (5)	0.5141 (2)	2.22 (10)
O4	0.1429 (3)	0.0404 (7)	0.7056 (2)	2.32 (10)
O3'	0.5192 (4)	-0.2587 (6)	1.2925 (2)	3.47 (14)
C1	0.5265 (5)	-0.2486 (8)	0.6709 (3)	2.19 (15)
C2	0.3554 (5)	-0.2455 (8)	0.5682 (3)	2.35 (15)
C3	0.1648 (5)	-0.2908 (6)	0.6140 (3)	1.72 (13)
C4	0.1458 (5)	-0.1690 (6)	0.7298 (3)	1.75 (14)
C5	0.3162 (5)	-0.2040 (5)	0.8340 (3)	1.57 (13)
C6	0.4934 (5)	-0.2390 (7)	0.8030 (3)	2.08 (15)

C1'	0.2791 (5)	-0.1864 (6)	0.9657 (3)	1.75 (14)
C2'	0.4227 (5)	-0.2367 (7)	1.0671 (3)	2.13 (15)
C3'	0.3831 (5)	-0.2220 (7)	1.1892 (3)	2.18 (15)
C4'	0.2001 (6)	-0.1628 (6)	1.2109 (3)	2.36 (17)
C5'	0.0598 (6)	-0.1105 (7)	1.1122 (3)	2.39 (16)
C6'	0.0972 (5)	-0.1195 (7)	0.9886 (3)	2.16 (16)

Table 2. Selected geometric parameters (Å, °)

O1—C1	1.226 (4)	C5—C6	1.345 (5)
O3—C3	1.425 (4)	C5—C1'	1.488 (5)
O4—C4	1.432 (4)	C1'—C2'	1.396 (5)
O3'—C3'	1.361 (4)	C1'—C6'	1.397 (5)
C1—C2	1.486 (5)	C2'—C3'	1.391 (5)
C1—C6	1.479 (5)	C3'—C4'	1.384 (5)
C2—C3	1.513 (5)	C4'—C5'	1.366 (6)
C3—C4	1.516 (5)	C5'—C6'	1.399 (5)
C4—C5	1.511 (5)		
O1—C1—C2	121.6 (3)	C6—C5—C1'	123.8 (3)
O1—C1—C6	119.2 (3)	C1—C6—C5	122.5 (3)
C2—C1—C6	119.2 (3)	C5—C1'—C2'	121.1 (3)
C1—C2—C3	112.9 (3)	C5—C1'—C6'	119.6 (3)
O3—C3—C2	107.8 (3)	C2'—C1'—C6'	119.3 (3)
O3—C3—C4	110.9 (3)	C1'—C2'—C3'	119.9 (3)
C2—C3—C4	110.8 (3)	O3'—C3'—C2'	123.0 (3)
O4—C4—C3	112.5 (3)	O3'—C3'—C4'	116.5 (3)
O4—C4—C5	105.9 (3)	C2'—C3'—C4'	120.4 (3)
C3—C4—C5	111.5 (3)	C3'—C4'—C5'	119.9 (3)
C4—C5—C6	118.5 (3)	C4'—C5'—C6'	120.8 (3)
C4—C5—C1'	117.6 (3)	C1'—C6'—C5'	119.5 (3)

Lorentz, polarization and secondary-extinction corrections were made. Full-matrix least-squares refinement was performed with non-H atoms anisotropic and anomalous dispersion for oxygen only. H atoms were found from a difference Fourier map. All H atoms attached to C atoms were calculated using idealized geometry (C—H = 0.95 Å) with *B*_{iso} adjusted to that of the attached C atom. H atoms involved in hydrogen bonding were initially refined and normalized in the final cycles (O—H = 0.95 Å) with *B*_{iso} adjusted as above. Using a previously refined Roger's (1981) parameter (including H atoms), a Bijvoet analysis similar to that used for sucrose (Hynes & Le Page, 1991) established the absolute configurations of C3 and C4 [BIJVOET utility in the NRCVAX package (Gabe, Le Page, Charland, Lee & White, 1989)]. The Roger's parameter $\eta = +0.992$ (near +1.0) indicates that the structure solution results in the correct absolute configuration. With calculated H atoms, $\eta = +0.877$. Out of 200 measurements, (*F*_o⁺ - *F*_o⁻) has the same sign as (*F*_c⁺ - *F*_c⁻) in 124 cases and the opposite sign in 76 cases. The robust probability of error (that the 3S and 4R absolute configurations are wrong) is 4.225 × 10⁻⁴.

The structure was solved by the direct methods program SHELXS86 (Sheldrick, 1985). Difference Fourier synthesis was carried out using NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989). The structures were drawn using ORTEP (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, hydrogen-bonding geometry, least-squares-planes data, and torsion angles have been deposited with the IUCr (Reference: CD1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Stable Ozonide

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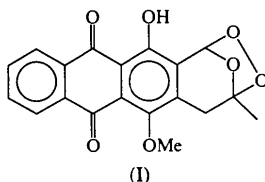
(Received 15 August 1994; accepted 15 September 1994)

Abstract

The title compound, 13-hydroxy-6-methoxy-4-methyl-4,5-dihydro-1,4-epoxy-1*H*-anthra[2,3-*d*][1,2]dioxepine-7,12(7*H*,12*H*)-dione, C₁₉H₁₄O₇, is an example of an ozonide which shows unusual stability. In contrast to other ozonides it is very resistant to reduction.

Comment

Anthracyclinones have emerged in recent years as important chemotherapeutic agents for the treatment of a wide range of carcinomas. These compounds contain the anthraquinone chromophore as part of a tetracyclic unit linked to a carbohydrate. In a series of experiments in this department directed towards the elaboration of an anthraquinone into daunomycin (Cambie, Larsen, Rutledge & Woodgate, 1987), an ozonide was obtained that proved to be extremely resistant to reduction. We report here the structure of that ozonide, (I).



An *ORTEP* (Johnson, 1965) diagram of the title compound showing the numbering scheme used is given in Fig. 1. The structure has the expected planar arrange-

ment of the aromatic system and there is a strong intramolecular hydrogen bond between the phenolic proton and the quinone O atom [O(1)···O(4) 2.538 Å], which is typical of hydroxyanthraquinone systems. There are structural details for 24 ozonides in the Cambridge Structural Database (Allen *et al.*, 1987) and analysis of these structures yields the following average dimensions: O—O 1.473 Å, C—(O—O) 1.443 Å and C—O 1.418 Å. These can be compared with the values obtained for the present structure: O—O 1.463 (3) Å, mean C—(O—O) 1.440 (2) Å and mean C—O 1.414 (3) Å. Many structures show marked asymmetry in the C—O bonds to the peroxy group and a similar feature is seen here: C(15)—O(5) 1.420 (4) Å and C(16)—O(6) 1.459 (3) Å. This asymmetry appears to be associated with other features of the molecule; here the shorter bond is to the C atom bound to the aromatic ring. Other distances and angles are within the normally expected range.

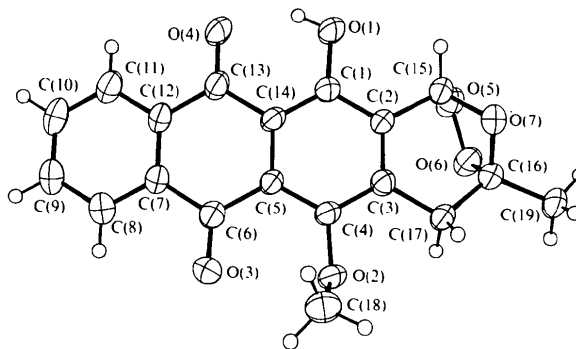


Fig. 1. The molecular structure (*ORTEP*; Johnson, 1965) showing 50% probability ellipsoids. H atoms are omitted for clarity.

Experimental

Crystal data

C₁₉H₁₄O₇
M_r = 354.30
Monoclinic
P2₁/c
a = 8.713 (4) Å
b = 11.5530 (10) Å
c = 15.612 (6) Å
β = 107.94 (5)°
V = 1495.1 (9) Å³
Z = 4
D_x = 1.574 Mg m⁻³

Cu Kα radiation
λ = 1.54180 Å
Cell parameters from 25 reflections
θ = 9.4–11.5°
μ = 1.029 mm⁻¹
T = 293 (2) K
Plates
0.28 × 0.22 × 0.08 mm
Orange

Data collection

Enraf–Nonius CAD-4
diffractometer
ω/2θ scans
Absorption correction:
none

R_{int} = 0.0249
θ_{max} = 50°
h = -9 → 9
k = 0 → 12
l = 0 → 17