

Fig. 2. Unit cell of the title compound projected down *a*. Dotted lines indicate hydrogen bonds. Molecules generated by the following symmetry operations are drawn: (I) x, y, z ; (II) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (III) $-x, 1-y, 1-z$; (IV) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

non-hydrogen atoms, the plane is fitted within $\sigma = 0.07$ Å. Separate least-squares planes through the phenyl ring C1–C6 and through the five/six-membered ring system C7–N15 are fitted within $\sigma = 0.009$ and $\sigma = 0.007$ Å respectively. The angle between these two planes is then 7.3 (8°).

From the *cis* arrangement of N15–H15 and O5 and the planarity of the molecule an intramolecular hydrogen bond N15–H15...O5 results with intra-

molecular contacts N15...O5 = 2.682 (2) and H15...O5 = 2.13 (3) Å.

The crystal structure is shown in Fig. 2 as a projection of the unit cell down *a*. An additional relatively weak intermolecular hydrogen bond N15–H15...N10ⁱ exists [symmetry operation (i): $x, \frac{3}{2}-y, \frac{1}{2}+z$; N15...N10ⁱ = 3.094 (3), H15...N10ⁱ = 2.39 (3) Å], connecting the molecules in the *c* direction. No further intermolecular contacts of interest were observed.

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Structure of an Oxatriquinane: *cis,anti,cis*-7b-Methylperhydrodicyclopenta[*b,d*]furan-1,6-dione

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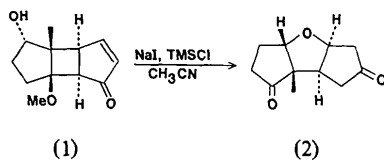
Abstract. C₁₁H₁₄O₃, $M_r = 194.23$, orthorhombic, $P2_12_12_1$, $a = 8.644$ (2), $b = 9.749$ (3), $c = 11.461$ (3) Å, $Z = 4$, $V = 965.8$ (5) Å³, $D_x(85\text{ K}) = 1.34\text{ g cm}^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.64\text{ cm}^{-1}$, $T = 85\text{ K}$, 1296 independent reflections, $F(000) = 416$, $R = 0.047$ for 1161 observed reflections with $I > 2.5\sigma(I)$. The compound, whose connectivity could not be determined from spectroscopic and chemical

information alone, is an oxa analogue of a linearly fused triquinane, with two *cis* ring fusions and an *anti* disposition of the rings at each end. All three rings possess slightly folded configurations typical of cyclopentanone and tetrahydrofuran systems.

Introduction. In the course of a study aimed at the preparation of highly functionalized hydrazulene systems for use in natural-product synthesis, we were exploring the reactions of a series of tricyclic pre-

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cursors containing cyclobutane rings. These systems were designed to be capable of opening an internal cyclobutane bond to give rise to the required seven-membered ring of the hydrazulene skeleton. However, treatment of enone (1) with a variety of reagents such as trimethylsilyl iodide led to high, and in some cases quantitative, yields of a highly crystalline saturated five-membered ring ketone with an exceptionally complicated proton NMR spectrum. Although the molecular formula could be determined to be $C_{11}H_{14}O_3$, no further unambiguous structural information was obtainable from these data alone. Thus an X-ray crystal structure determination was carried out, resulting in the unusual structure shown below (2). The compounds were isolated as racemic mixtures; for convenience just one stereoisomer is shown for each, below.

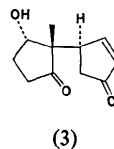


Experimental. Compound (2), colorless prisms obtained by direct sublimation upon purification by gas chromatography, crystal dimensions $0.26 \times 0.32 \times 0.36$ mm; Syntex $P2_1$ diffractometer, locally constructed low-temperature apparatus based upon an Enraf–Nonius design, $T = 85$ K, Mo $K\alpha$ radiation, graphite monochromator; cell dimensions from least-squares fit of ten reflections with $18 < 2\theta < 26^\circ$; space group $P2_12_12_1$ (No. 19) based on conditions $00l, l = 2n; 0k0, k = 2n; h00, h = 2n$; no absorption correction (range of absorption correction factors 1.01–1.02); data collected to $2\theta_{\max} = 55^\circ$ with hkl ranges 0 to 11, 0 to 12, and 0 to 14, respectively; ω scans, 1° range, 8° min^{-1} , $\pm 1^\circ$ offset for backgrounds; two check reflections monitored every 200 reflections showed no decay; 1405 reflections measured, 1296 independent data, 1161 observed [$I > 2.5\sigma(I)$] used in the solution and refinement (based on F); structure solved by direct methods; full-matrix least-squares refinement, 99 parameters; all atoms with isotropic thermal parameters, those of H atoms fixed at $U = 0.02 \text{ \AA}^2$; $R = 0.047$, $wR = 0.052$, $w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$, $S = 1.868$, $(\Delta/\sigma)_{\max} = 0.017$ for y of C(7); $(\Delta/\sigma)_{\text{ave}} = 0.004$; $\Delta\rho$ excursions in difference map between 0.40 and -0.53 e \AA^{-3} , respectively; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs from the *SHELXTL* (version 3) package (Sheldrick, 1981).

Discussion. Crystallization of compound (2) resulted in spontaneous resolution. The final atomic coordinates and isotropic thermal parameters are given in Table 1

and bond angles and bond distances are listed in Table 2.* The structure of (2) (Fig. 1) consists of discrete molecules containing the perhydrocyclopenta[b,d]-furan ring system, essentially a dicyclopentyl ether with a central ring closed by an additional C–C bond. Two relatively normal cyclopentanone ketone carbonyl groups are present with C(1)–O(1) being 1.209 (4) and C(10)–O(2) 1.213 (3) Å. Internal ring angles at these carbonyl carbons are C(2)–C(1)–C(5) 109.6 (2) and C(6)–C(10)–C(9) 110.1 (2)°. Bond lengths to the central ring oxygen are C(3)–O(3) 1.447 (3) and C(7)–O(3) 1.456 (3) Å, and the C(3)–O(3)–C(7) angle is 110.9 (2)°. The ring system possesses two *cis* ring fusions, *anti* to one another; this is most readily seen in Fig. 2. All three rings are non-planar, although none possesses the distinctive envelope conformation typical of isolated, saturated five-membered rings (see below). A certain amount of opening of bond angles due to steric interference is seen at the carbons of the ring fusions. This is most noticeable at the quaternary carbon, C(6), about which the bond angles range from 102.9 (2) to 116.1 (2)°. This is the first X-ray structure determination of a compound containing this oxatricyclic skeleton. In fact, there are only two previous appearances of derivatives of this ring system in the literature (Levina, Tautsyreva, Vinogradova & Treshchova, 1952; Alder & Flock, 1956). However, an X-ray structure determination has been carried out on an all-carbon analogue; comparisons between the structures are presented below.

The pathway to (2) presumably involves a Lewis-acid-catalyzed retro-aldol fragmentation of the *external* cyclobutane bond [bottom center, structure (1)] between the carbons α and β to the carbonyl group. This leads to a dicyclopentyl derivative (3), which can readily close to (2) *via* Michael addition of the free hydroxyl on one ring to the enone system of the other.



Part of our interest in this transformation lies in the resemblance of (2) to members of the class of naturally occurring compounds known as linearly fused triquinanes, which contain the all-carbon analogue of this tricyclic ring system (Paquette, 1979, 1984). Most notable is the similarity of (2) in both substitution pattern and stereochemistry to the hirsutanes, which

* Lists of structure factors, H-atom coordinates, bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44029 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$)

	x	y	z	$U(\text{\AA}^2)$
O(1)	4754 (3)	1855 (2)	10274 (2)	27 (1)
O(2)	7030 (2)	1600 (2)	4793 (2)	22 (1)
O(3)	6305 (2)	4392 (2)	7430 (2)	16 (1)
C(1)	5134 (3)	2151 (3)	9290 (3)	19 (1)
C(2)	4285 (4)	3167 (3)	8511 (3)	22 (1)
C(3)	5241 (3)	3248 (3)	7386 (2)	16 (1)
C(4)	6265 (3)	1954 (3)	7358 (2)	15 (1)
C(5)	6520 (3)	1581 (3)	8648 (2)	17 (1)
C(6)	7712 (3)	2455 (3)	6722 (2)	14 (1)
C(7)	7859 (3)	3965 (3)	7100 (2)	15 (1)
C(8)	8402 (3)	4748 (3)	6022 (3)	17 (1)
C(9)	7601 (3)	4036 (3)	4997 (2)	18 (1)
C(10)	7391 (3)	2568 (3)	5400 (2)	16 (1)
C(11)	9178 (4)	1601 (3)	6902 (3)	19 (1)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

O(1)–C(1)	1.209 (4)	O(2)–C(10)	1.213 (3)
O(3)–C(3)	1.447 (3)	O(3)–C(7)	1.456 (3)
C(1)–C(2)	1.522 (4)	C(1)–C(5)	1.512 (4)
C(2)–C(3)	1.534 (4)	C(3)–C(4)	1.541 (4)
C(4)–C(5)	1.538 (4)	C(4)–C(6)	1.529 (4)
C(6)–C(7)	1.540 (4)	C(6)–C(10)	1.545 (4)
C(6)–C(11)	1.530 (4)	C(7)–C(8)	1.526 (4)
C(8)–C(9)	1.530 (4)	C(9)–C(10)	1.515 (4)
C(3)–O(3)–C(7)	110.9 (2)	O(1)–C(1)–C(2)	124.8 (3)
O(1)–C(1)–C(5)	125.5 (3)	C(2)–C(1)–C(5)	109.6 (2)
C(1)–C(2)–C(3)	105.5 (2)	O(3)–C(3)–C(2)	110.6 (2)
O(3)–C(3)–C(4)	105.5 (2)	C(2)–C(3)–C(4)	106.6 (2)
C(3)–C(4)–C(5)	104.8 (2)	C(3)–C(4)–C(6)	102.6 (2)
C(5)–C(4)–C(6)	114.6 (2)	C(1)–C(5)–C(4)	105.5 (2)
C(4)–C(6)–C(7)	103.8 (2)	C(4)–C(6)–C(10)	110.1 (2)
C(7)–C(6)–C(10)	102.9 (2)	C(4)–C(6)–C(11)	116.1 (2)
C(7)–C(6)–C(11)	114.5 (2)	C(10)–C(6)–C(11)	108.7 (2)
O(3)–C(7)–C(6)	105.7 (2)	O(3)–C(7)–C(8)	110.6 (2)
C(6)–C(7)–C(8)	106.0 (2)	C(7)–C(8)–C(9)	104.8 (2)
C(8)–C(9)–C(10)	104.4 (2)	O(2)–C(10)–C(6)	123.6 (2)
O(2)–C(10)–C(9)	126.2 (2)	C(6)–C(10)–C(9)	110.1 (2)

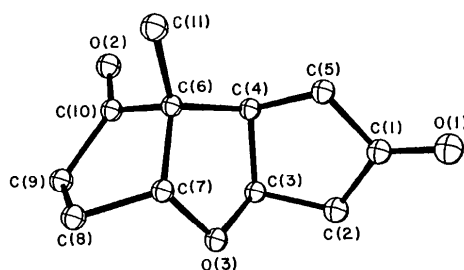


Fig. 1. A view of the title compound with atomic numbering.

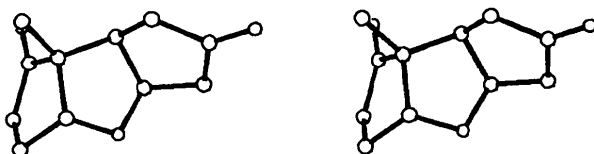
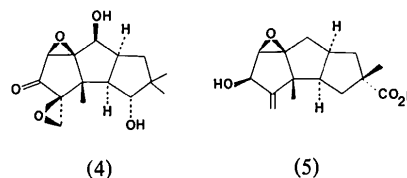


Fig. 2. Stereoview of the title compound.

include the intriguing anti-tumor agent coriolin (4), and another closely related compound, hirsutic acid (5). An



X-ray structure determination on the latter (Comer & Trotter, 1966) reveals many points of similarity between it and (2). Both have the same overall stereochemical characteristics with respect to the ring fusions. In (5) as in (2) the rings are all non-planar, although (5) does exhibit the envelope conformation for the saturated ring containing the acid function. Otherwise the framework geometries are very similar, even to the detailed bond angles about the ring-fusion carbons. For example, in (5) four of the six angles about the carbon that corresponds to C(6) in compound (2) are within 1° of their counterparts. The remaining two angles, corresponding to C(4)–C(6)–C(11) and C(10)–C(6)–C(11) in (2), are 110.8 and 114.2° , respectively [compare 116.1 and 108.7° in (2)], which represents nothing more than a small displacement in the position of the angular methyl group that does not affect the overall shape of the molecule to any significant extent. The ease of synthetic access to (2) gives rise to the possibility of preparing 'oxatriquinane' analogues of a number of these systems for appropriate biological testing. The overall shape similarities between the groups of compounds as revealed in this structure determination make this a particularly promising area for future study.

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