Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.7365P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.124$	$\Delta\rho_{max} = 0.282$ e Å^{-3}
$S = 1.129$	$\Delta\rho_{min} = -0.282$ e Å^{-3}
3011 reflections	Extinction correction: none
191 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H-atom parameters constrained	

Table 1. *Selected geometric parameters (Å, °)*

S1—C18	1.753 (2)	C9—C10	1.386 (3)
S1—C3	1.760 (2)	C10—C11	1.481 (3)
C1—C2	1.399 (3)	C11—C12	1.387 (3)
C1—C6	1.414 (3)	C11—C20	1.430 (3)
C1—C10	1.428 (3)	C12—C13	1.398 (3)
C2—C3	1.378 (3)	C13—C14	1.372 (4)
C2—C19	1.407 (3)	C14—C15	1.403 (3)
C3—C4	1.415 (3)	C15—C20	1.410 (3)
C4—C5	1.364 (3)	C15—C16	1.434 (3)
C5—C6	1.435 (3)	C16—C17	1.367 (3)
C6—C7	1.407 (3)	C17—C18	1.410 (3)
C7—C8	1.369 (4)	C18—C19	1.382 (3)
C8—C9	1.401 (4)	C19—C20	1.397 (3)
C18—S1—C3	92.17 (11)	C19—C18—S1	110.0 (2)
C2—C3—S1	109.8 (2)	C17—C18—S1	131.6 (2)
C4—C3—S1	131.7 (2)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1306). Services for accessing these data are described at the back of the journal.

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cis-3,5a-Dimethyl-1-oxo-5a,6,8,9-tetrahydro-1*H*,7*H*-pyrano[4,3-*b*][1]benzopyran-6-yl Formate

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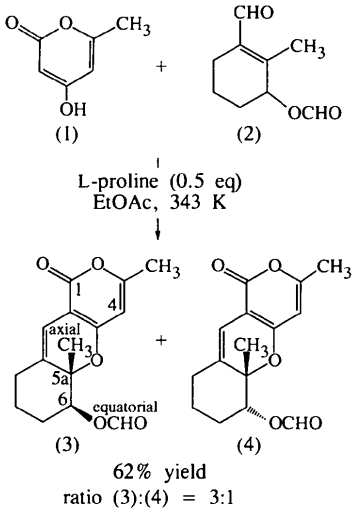
Abstract

Characterization of the title compound, $C_{15}H_{16}O_5$, by X-ray diffraction affirms its linearly fused tricyclic structure and the chair conformation of the cyclohexane ring on which the methyl and adjacent formyloxy groups are *cis*, the former being axial and the latter equatorial. The C=C bond γ,δ to the carbonyl is longer, while the C=C bond α,β to the carbonyl is shorter than their counterparts in a 3-substituted 4-hydroxy-6-methyl-2-pyrone.

Comment

In studies of the synthesis of (+)-pyripyropene A (Tomoda *et al.*, 1994) and structurally related biologically active compounds (Omura *et al.*, 1995), a new condensation reaction leading to the polycyclic pyran ring system was developed. (+)-Pyripyropene A is a

potent inhibitor of acyl-CoA:cholesterol acyltransferase (ACAT), a microsomal enzyme that converts cholesterol to cholesterol esters. Inhibitors of ACAT may be useful in the treatment of hypercholesterolemia and atherosclerosis (Sliskovic & White, 1991). Treatment of 4-hydroxy-6-methyl-2-pyrone, (1), with 3-formyloxy-2-methyl-1-cyclohexenecarboxaldehyde, (2), and L-proline in ethyl acetate at 343 K provided the tricyclic pyrone *cis*-3,5a-dimethyl-1-oxo-5a,6,8,9-tetrahydro-1*H*,7*H*-pyrano[4,3-*b*][1]benzopyran-6-yl formate, (3), and its *trans* isomer, (4), in a ratio of 3:1, which were separated by column chromatography. The relative stereochemistry at C5a and C6 of (3) was determined by single-crystal X-ray analysis, which also showed its linearly fused tricyclic structure. This condensation reaction of a variety of other substituted pyrones with various cyclohexenecarboxaldehydes provided products whose spectral data (^{1}H and ^{13}C NMR, *etc.*) were in agreement with those of (3). This class of tricyclic pyrones exhibits various types of important biological activity, including the inhibition of DNA synthesis and tumor-cell growth *in vitro* (Perchellet *et al.*, 1997).



A view of molecule (3) with its atom numbering is shown in Fig. 1. The cyclohexane ring is in a chair conformation, the C5a methyl group is axial and the C6 formyloxy equatorial. The pyran and pyrone rings are coplanar. Bonds C1—O2 [1.392 (2) Å] and C4a—C10a [1.362 (2) Å] are longer than the corresponding O1—C2 [1.381 (3) Å] and C3—C4 [1.341 (3) Å] bonds of a 2*H*-2-pyranone described by Kálmán *et al.* (1988). Although the C3—C4 bond [1.341 (3) Å] is longer and the C4a—C10a bond [1.362 (2) Å] is shorter than the corresponding C5—C6 [1.321 (9) Å] and C3—C4 [1.398 (8) Å] bonds of a 3-substituted 4-hydroxy-6-methyl-2-pyrone reported by Thailambal, Pattabhi & Gabe (1986), the bond angles of the pyrone ring of their compound are similar to those of (3).

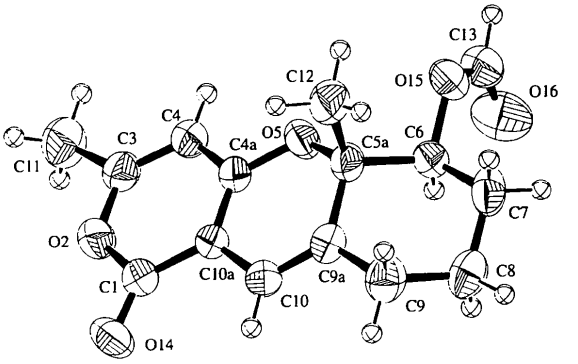


Fig. 1. The molecular structure and atom-numbering scheme for (3) with displacement ellipsoids at the 50% probability level.

Experimental

Synthesis of the title compound, (3), and its C5a,6-*trans*-isomer, (4), was achieved by the condensation of 147 mg (0.88 mmol) of 3-formyloxy-2-methyl-1-cyclohexenecarboxaldehyde, (2), and 110 mg (0.88 mmol) of pyrone (1) in the presence of 50 mg (0.4 mmol) of L-proline in 10 ml of ethyl acetate under argon at 298 K for 1 d, in a 313 K bath for 3 d and a 343 K bath for 1 d. The mixture, diluted with 120 ml of methylene chloride, was washed with 50 ml of saturated aqueous $NaHCO_3$, then with 50 ml of brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and diethyl ether as eluant, to give 113 mg (46.5% yield) of (3) and 38 mg (15.5% yield) of (4). Both products displayed satisfactory ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), UV, IR and low-resolution mass spectra, and elemental analyses. Crystallized (3) [from diethyl ether–hexane (1:1); m.p. 411–413 K] was used for the X-ray study.

Crystal data

$C_{15}H_{16}O_5$
M_r = 276.29
Triclinic
$P\bar{1}$
a = 9.1708 (14) Å
b = 10.6960 (3) Å
c = 7.4317 (15) Å
α = 92.08 (2)°
β = 107.80 (1)°
γ = 92.57 (2)°
V = 692.4 (3) Å^3
Z = 2
D_x = 1.3252 (6) Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 16.96–19.08°
μ = 0.10 mm^{-1}
T = 296 K
Irregular fragment
0.46 × 0.41 × 0.27 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 4° min^{-1} in ω)
Absorption correction: none
2601 measured reflections
2433 independent reflections
1619 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

θ_{max} = 25.01°
h = 0 → 10
k = −12 → 12
l = −8 → 8
3 standard reflections every 150 reflections
intensity decay: 3.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.1711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F) = 0.038$	$(\Delta/\sigma)_{max} = -0.001$
$wR(F^2) = 0.103$	$\Delta\rho_{max} = 0.214$ e Å^{-3}
$S = 1.093$	$\Delta\rho_{min} = -0.187$ e Å^{-3}
2433 reflections	Extinction correction: none
183 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H-atom parameters constrained	

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN* and *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN* and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*93 and *PLATON* (Spek, 1990).

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5,11,17,23-Tetra-*tert*-butyl-26,28-dihydroxy-25,27-bis[2-(*p*-nitrobenzylideneamino)-ethoxy]calix[4]arene

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Abstract

The title compound, $C_{62}H_{72}N_4O_8$, has a cone conformation. The planes of the individual phenyl rings are inclined at angles of 97.49 (7), 142.24 (10), 92.78 (7) and 143.14 (11)° to the plane of the methylene C atoms linking these aromatic rings. There are intramolecular hydrogen bonds between the proximal hydroxy and ether functional groups, with O···O non-bonded contacts of 2.862 (3) and 2.892 (3) Å, respectively. The cones are linked to one another along the *a* axis by two weak intermolecular C—H···O hydrogen bonds [C···O contacts of 3.303 (7) and 3.377 (7) Å] to form an infinite polymeric chain.

Comment

Calixarenes are currently enjoying considerable interest in the field of supramolecular chemistry because their derivatives can form inclusion complexes with cations or with neutral molecules (Gutsche, 1989; Vicens & Böhmer, 1991). As a result of selective 1,3-dialkylation of *p-tert*-butylcalix[4]arene (Gutsche, 1989; Vicens & Böhmer, 1991), conformationally stable modified tetrameric structures with the 2+2′ functional group disposition and distal 1,3-regiochemistry have been developed. They are synthesized by treatment of *p-tert*-butylcalix[4]arene with various electrophiles such as ethyl bromoacetate, chloroacetone, bromopinacolone and chloroacetonitrile under basic conditions (Collins, McKervey & Harris, 1989; Collins *et al.*, 1991). We report here an efficient method for synthesizing the title compound, (I), by reacting *p*-nitrobenzaldehyde with calix[4]areneamine.