Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD-4 Software.* Version 5. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* A43, C-294.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kojic-Prodic, B., Ruzic-Toros, Z. & Sunjic, V. (1984). *Helv. Chim. Acta,* 67, 916–926.

Kumaradhas, P., Nirmala, K. A. & Ravikumar, K. (1995). *Acta Cryst.* C51, 1932–1934.

Mitchell, L. B., Schroeder, J. S. & Mason, J. W. (1982). *Am. J. Cardiol.* 49, 629–635.

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.

Parisi, A. F., Strauss, W. E., Melntyre, K. M. & Sasahara, A. A. (1982). *Circulation,* 65, 38–42.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Product of a Novel Carbocyclic Enlargement in Aqueous Media: 9β-tert-Butoxy-4-(E)-ethylidene-8β-methyl-5-oxobicyclo[6.3.0]undecan-2β-carboxylic Acid Methyl Ester

Joel T. Mague, Chao-Jun Li, Dong-Li Chen, Yue-Qi Lu and John X. Haberman

Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. E-mail: joelt@mailhost.tcs.tulane.edu

Abstract

The title compound, $C_{20}H_{32}O_4$, is the major diastereomer obtained by the two-carbon ring expansion of a precursor containing fused five- and six-membered rings. It is shown to have the methyl, *tert*-butoxy and carboxymethyl substituents in mutually *cis* dispositions.

Comment

The formation of carbocycles having medium-to-large ring sizes is of great significance since such species constitute the structural core of many biologically important natural products (Devon & Scott, 1972).

As ring-expansion methodologies allow one to avoid the unfavourable entropic factors associated with other routes to medium- and large-ring carbocycles (Dowd & Zhang, 1993; Hesse, 1991; Roxburgh, 1993; Stach & Hesse, 1988), development of efficient procedures of this type is an area of continuing interest. We have recently reported an efficient and general procedure for the two-atom carbocyclic enlargement in aqueous media which is effective for both simple and fused ring systems (Li, Chen, Lu, Haberman & Mague, 1996). In order to define unequivocally the stereochemistry of the major product (1) obtained from the ring-expansion of (2), the structure of (1) was determined.

(1)　　　　　　(2)
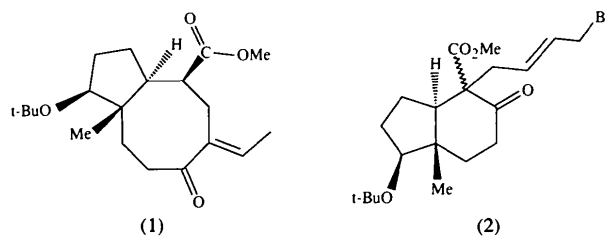
The results demonstrate that the ester functionality is disposed *cis* to the methyl group attached to the ring junction (C2) as well as to the *tert*-butoxy group on C11 of the five-membered ring. The C4–C7, C12, O4 unit is planar within experimental error with C13 0.034 (4) Å out of this plane while the distances and angles associated with it compare favorably with those in related molecules (Ivie, Watson & Dominguez, 1974; Theocharis, Nakanishi & Jones, 1981). All other geometric parameters appear normal. The *trans* ring fusion in (2) is maintained in (1) and there are no unusual intermolecular contacts.
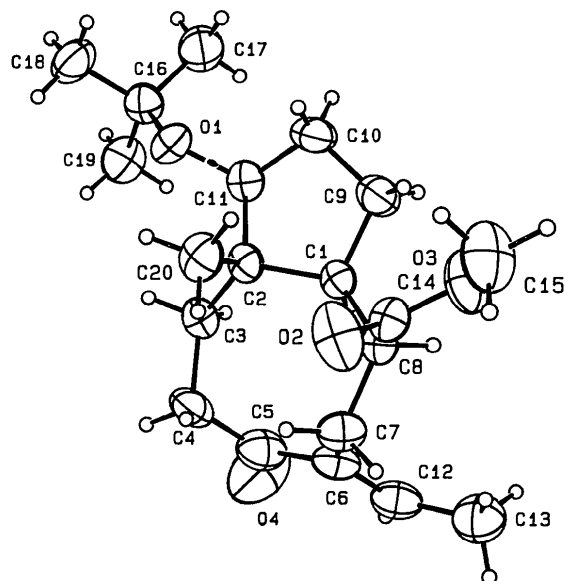

Fig. 1. A perspective view of (1). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which for clarity are arbitrarily small.

Experimental

A colourless crystal of (1), prepared by the reported method (Li, Chen, Lu, Haberman & Mague, 1996) and obtained by slow evaporation of a hexane/ethyl acetate solution of the compound, was cut to size and mounted on a thin glass fibre with epoxy cement.

Crystal data

$C_{20}H_{32}O_4$	Mo $K\alpha$ graphite-
$M_r = 336.48$	monochromated radiation
Orthorhombic	$\lambda = 0.71073$ Å
$P2_12_12_1$	Cell parameters from 25
$a = 5.8088\,(3)$ Å	reflections
$b = 17.976\,(2)$ Å	$\theta = 10–15°$
$c = 18.213\,(2)$ Å	$\mu = 0.075$ mm^{-1}
$V = 1901.8\,(5)$ Å^3	$T = 293$ K
$Z = 4$	Block
$D_x = 1.1175$ Mg m^{-3}	$0.46 \times 0.33 \times 0.30$ mm
D_m not measured	Colourless

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 24.95°$
diffractometer	$h = 0 \rightarrow 6$
$\theta/2\theta$ scans	$k = 0 \rightarrow 21$
Absorption correction:	$l = 0 \rightarrow 21$
none	2 standard reflections
1948 measured reflections	frequency: 120 min
1948 independent reflections	intensity decay: <1%
1475 observed reflections	
$[I > 2.0\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.087$
$R = 0.043$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
$wR = 0.060$	$\Delta\rho_{min} = -0.11$ e Å^{-3}
$S = 2.006$	Extinction correction: none
1475 reflections	Atomic scattering factors
217 parameters	from *International Tables*
H-atom parameters not	*for X-ray Crystallography*
refined	(1974, Vol. IV)
$w = 4F_o^2/[\sigma^2(F_o^2)$	
$+ 0.0016F_o^4]$	

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.3745 (4)	0.3927 (1)	0.9189 (1)	0.0467 (6)
O2	0.0089 (5)	0.1819 (1)	0.7201 (2)	0.0685 (8)
O3	0.2440 (4)	0.0930 (1)	0.7573 (2)	0.0635 (7)
O4	0.7828 (6)	0.3995 (2)	0.6072 (2)	0.105 (1)
C1	0.5135 (5)	0.2535 (2)	0.7780 (2)	0.0354 (7)
C2	0.4021 (5)	0.3296 (2)	0.8000 (2)	0.0366 (8)
C3	0.4860 (7)	0.3974 (2)	0.7564 (2)	0.0450 (8)
C4	0.4371 (7)	0.4059 (2)	0.6738 (2)	0.055 (1)
C5	0.6143 (8)	0.3656 (2)	0.6292 (2)	0.059 (1)
C6	0.5877 (6)	0.2843 (2)	0.6132 (2)	0.0453 (9)
C7	0.3798 (6)	0.2438 (2)	0.6410 (2)	0.0472 (9)
C8	0.4182 (5)	0.2040 (2)	0.7150 (2)	0.0363 (8)
C9	0.5411 (7)	0.2095 (2)	0.8494 (2)	0.056 (1)
C10	0.4915 (8)	0.2613 (2)	0.9118 (2)	0.056 (1)
C11	0.5004 (7)	0.3385 (2)	0.8789 (2)	0.0420 (8)
C12	0.7536 (7)	0.2511 (2)	0.5741 (2)	0.0532 (9)
C13	0.7640 (8)	0.1718 (3)	0.5530 (2)	0.069 (1)
C14	0.2004 (6)	0.1611 (2)	0.7320 (2)	0.0401 (8)
C15	0.0431 (8)	0.0472 (2)	0.7709 (3)	0.074 (1)
C16	0.4986 (7)	0.4422 (2)	0.9684 (2)	0.0478 (9)
C17	0.6490 (8)	0.4004 (2)	1.0210 (2)	0.068 (1)
C18	0.3098 (8)	0.4810 (2)	1.0089 (2)	0.065 (1)
C19	0.6398 (8)	0.4975 (2)	0.9238 (2)	0.064 (1)
C20	0.1384 (6)	0.3287 (2)	0.8028 (2)	0.052 (1)

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

O4—C5	1.221 (5)	C6—C7	1.498 (5)
C3—C4	1.539 (5)	C6—C12	1.339 (6)
C4—C5	1.498 (6)	C7—C8	1.543 (5)
C5—C6	1.498 (6)	C12—C13	1.478 (7)
C3—C4—C5	110.8 (3)	C5—C6—C12	117.6 (4)
O4—C5—C4	119.2 (4)	C7—C6—C12	122.9 (4)
O4—C5—C6	120.4 (4)	C6—C7—C8	113.8 (3)
C4—C5—C6	120.4 (4)	C6—C12—C13	126.7 (4)
C5—C6—C7	119.5 (4)		
C15—O3—C14—C8	176.7 (3)	C4—C5—C6—C7	1.2 (5)
C8—C1—C2—C3	-86.4 (4)	C4—C5—C6—C12	-179.0 (3)
C9—C1—C8—C7	178.8 (3)	C5—C6—C7—C8	-95.0 (4)
C11—C2—C3—C4	175.8 (3)	C12—C6—C7—C8	85.2 (4)
C3—C4—C5—C6	85.2 (4)	C5—C6—C12—C13	179.1 (4)
O4—C5—C6—C7	179.8 (4)	C7—C6—C12—C13	-1.1 (6)
O4—C5—C6—C12	-0.3 (5)	C6—C7—C8—C14	-175.5 (3)

General procedures for crystal orientation, unit-cell determination and refinement, and data collection have been published (Mague & Lloyd, 1989). The space group was uniquely determined by the observed systematic absences and all but two of the non-H atoms were located in the initial E map. The remainder were found from a $\Delta\rho$ map following initial full-matrix least-squares refinement. Most H atoms were located in a $\Delta\rho$ map following refinement of all non-H atoms with anisotropic displacement parameters. As a result of the small size of the data set and since these initial positions indicated no unusual geometric features, the H atoms were included as fixed contributions in calculated positions (C—H = 0.95 Å) with isotropic displacement parameters 20% larger than those of the attached C atoms and updated periodically. No distinction between enantiomers could be made on the basis of refinement so the original choice was retained.

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: Direct methods (*SIR*88; Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX MolEN*.

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Devon, T. K. & Scott, A. I. (1972). In *Handbook of Naturally Occurring Compounds*, Vol. II. New York and London: Academic Press.

Dowd, P. & Zhang, W. (1993). *Chem. Rev.* **93**, 2091–2115.

Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Hesse, M. (1991). In *Ring Enlargement in Organic Chemistry.* Weinheim: VCH.

Ivie, R. A., Watson, W. H. & Dominguez, X. A. (1974). *Acta Cryst.* **B30**, 2891–2893.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Li, C.-J., Chen, D.-L., Lu, Y.-Q., Haberman, J. X. & Mague, J. T. (1996). *J. Am. Chem. Soc.* **118**, 4216–4217.

Mague, J. T. & Lloyd, C. L. (1989). *Organometallics,* **7**, 983–993.

Roxburgh, C. J. (1993). *Tetrahedron,* **49**, 10749–10784.

Stach, H. & Hesse, M. (1988). *Tetrahedron,* **44**, 1573–1590.

Theocharis, C. R., Nakanishi, H. & Jones, W. (1981). *Acta Cryst.* **B37**, 756–758.

2,4,6-Triphenyl-4*H*-pyran-3,5-dicarbox-aldehyde

S. SELLADURAI,[a] R. MURUGESAN,[a] K. SUBRAMANIAN,[a] Y. S. CHEN,[b] S. NARASINGA RAO[b] AND ELIZABETH M. HOLT[c]

[a]*Department of Physics, Anna University, Madras 600 025, India,* [b]*Department of Physics, University of Central Oklahoma, Edmond, Oklahoma, USA, and* [c]*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@osucc.bitnet*

Abstract

The structure of 2,4,6-triphenyl-4*H*-pyran-3,5-dicarbox-aldehyde, $C_{25}H_{18}O_3$, a potential fungicide, has a pyran ring in a flattened boat conformation, with the C4 and O3 atoms displaced from the basal plane by 0.299 and 0.159 Å, respectively. The aldehyde groups display an *ap* orientation with respect to the double bonds of that plane.

Comment

Pyran derivatives have shown biological activity as fungicides and insecticides. In particular, pyran derivatives have shown activity against the growth of *Pyricularia Oryzae cav.*, a virulent systemic fungus observed in rice plants and responsible for significant yield losses in temperate climates. In an effort to maximize the activity of the antifungicide, studies of the activity of substituted pyran molecules have been undertaken. In these studies, chloropyran derivatives have shown greater activity than the parent compound, pyran, or its methoxy- or benzo-substituted modifications.

We have determined the solid-state structure of the 2,4,6-triphenyl-3,5-dicarboxaldehyde derivative of pyran, (I), as part of a study linking the structure and activity of the compounds of this family, in an effort to understand the geometry of the receptor site.
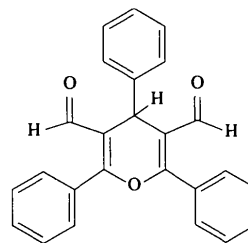
(I)

Pyran rings normally adopt a flattened boat conformation, but there is considerable variation in the flatness of such a hetero-ring. Measures of flatness are (i) the distance of the O and C4 atoms from the plane of the base of the boat (atoms C2, C3, C5 and C6) and (ii) the sum of the absolute values of the intra-ring torsion angles which should be zero for a totally planar ring and 360° for an idealized boat conformation.

In the title compound, (I), the pyran ring exists with the C2=C3 and C5=C6 double bonds coplanar (deviation 0.013 Å) and the O3 and C4 atoms displaced from this plane by 0.159 and 0.299 Å, respectively (Fig. 1). The sum of the intra-ring torsion angles is 88.7°. These values may be compared with the similar degree of nonplanarity observed in 2-amino-3-cyano-4-isopropyl-5-cyano-6-methyl-4*H*-pyran [deviations of the O1 and C4 atoms from the basal plane are −0.154 (1) and −0.301 Å, respectively; the sum of the intra-ring torsion angles is 89.0°] (Bellanato, Florencio, García-Blanco, Martin & Seoane, 1987), and the greater planarity of the pyran rings in both 2-amino-6-chloromethyl-3-cyano-5-ethoxycarbonyl-4-(2-furyl)-4*H*-pyran [O1 and C4 are −0.125 (2) and −0.265 (2) Å, respectively, from the basal plane and the torsion angle sum is 77.9°] (Lokaj, Kettmann, Pavelčík, Ilavský & Marchalín, 1990) and 2-amino-3-ethoxycarbonyl-4-phenyl-5-cyano-6-phenyl-4*H*-pyran [O1 and O4 are −0.095 (7) and −0.198 (7) Å, respectively, from the basal plane and the torsion angle sum is 67.5°] (Bellanato, Florencio, Martin & Seoane, 1988). 2,6-Dimethyl-4-phenyl-4*H*-pyran-3,5-dicarbonitrile, in comparison, crystallizes with a more planar pyran ring (O1 and C4 are −0.0334 and −0.0762 Å, respectively, from the basal plane and the torsion angle sum is 22.3°) (Florencio & García-