Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. Cambridge, England.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. Göttingen, Deutschland.
Zaprutko, L. (1994*a*). *Pol. J. Chem.* **68**, 665–673.
Zaprutko, L. (1994*b*). *Pol. J. Chem.* **68**, 1753–1765.
Zaprutko, L., Gzella, A. & Wrzeciono, U. (1990). *Liebigs Ann. Chem.* pp. 373–378, und dort zitierte Literatur.

Acta Cryst. (1995). C**51**, 912–914

Product of an S_N2' Ring-Opening Reaction, (1*R**,2*R**,3*R**,4*R**,7*R**)-2,4,7-Trimethylcyclohept-5-ene-1,3-diol

JOHN COLUCCI, CHRISTOPHER GAJDA, MARK LAUTENS AND ALAN J. LOUGH

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

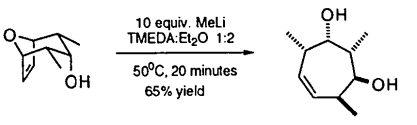
(*Received* 5 *August* 1994; *accepted* 30 *September* 1994)

Abstract

The relative stereochemistry of the title compound, $C_{10}H_{18}O_2$, has been confirmed. The geometry of the seven-membered ring indicates that it is strained. Molecules are linked by O—H···O hydrogen bonds [O···O 2.796 (3) and 2.816 (3) Å] about independent $\bar{4}$ inversion sites to form infinite columns with two independent $(\cdots O—H\cdots O—H\cdots)_2$ rings.

Comment

It has been shown that treatment of the [3.2.1]-oxabicyclic compound (1), 2,7-dimethyl-3,6-epoxycyclohept-4-enol, with excess methyllithium in TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) can promote a formal S_N2' ring-opening reaction to yield the cycloheptene compound (2) (Lautens, Abd-El-Aziz & Lough, 1990). It was noted, however, that this ring opening could be accomplished only if the stereochemistry of the hydroxyl group was *endo* and if it was unprotected. Other organolithium compounds reacted much more generally. Earlier studies established that *tert*-butyllithium reacted exclusively from the *exo* face of the olefin. It was essential, therefore, to determine if methyllithium would attack from the same face in spite of this peculiar 'alkoxide effect'. The crystal structure of compound (2) did, indeed, show that attack occurred, as it did with other organolithiums, from the *exo* face of the olefin only. It is with the knowledge of the relative substitution pattern of the five substituents on cycloheptene ring of (2) that our ongoing syntheses of natural products such as ionomycin and bourgeanic acid can be undertaken.



(1) (2)

The cycloheptene ring of the title molecule (Fig. 1) adopts a chair-type conformation with atoms C1, C7, C3 and C4 forming a plane [mean deviation 0.022 (2) Å]. Atom C2 is 0.686 (4) Å 'above' this plane and atoms C5 and C6 are −0.919 (4) and −0.939 (4) Å, respectively, 'below' this plane. The strain present in the molecule is reflected in the deviations from standard values of the internal angles of the cycloheptene ring, which, on the principles of hybridization, are all slightly larger than would be expected. The most prominent deviations are shown by the angle C5—C6—C7 [127.1 (3)°] for an sp^2-hydridized C atom and the angle C2—C1—C7 [117.9 (2)°] for an sp^3-hybridized C atom.

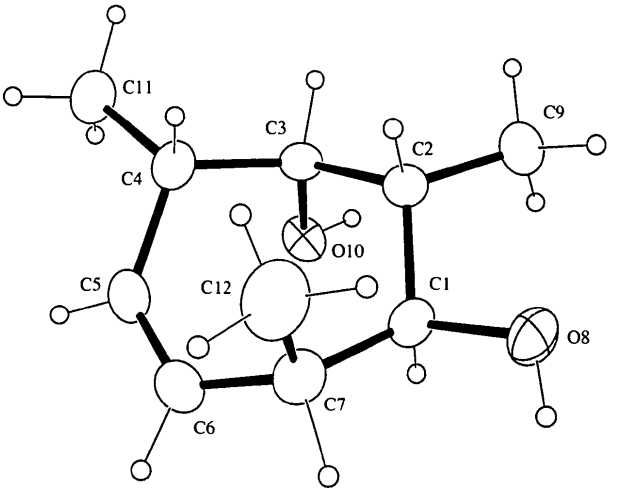


Fig. 1. A view of compound (2) with the crystallographic numbering scheme. Displacement ellipsoids are at the 25% level and H atoms are shown as spheres of arbitrary size.

Hydrogen-bonded $(\cdots O—H\cdots O—H\cdots)_2$ rings are formed by molecules related by fourfold inversion centers. Both of the hydroxyl groups present in the molecule are involved in this type of cyclic hydrogen bonding, alternating about different $\bar{4}$ centers which are situated every $\frac{1}{2}$ unit cell along the **z** direction (a virtue of the *I*-centering). Molecules are linked *via* this hydrogen bonding to produce infinite columns (see Fig. 2). The unique close intermolecular distances are O8···O8($\frac{1}{4}-y$, $\frac{1}{4}+x$, $\frac{1}{4}-z$) 2.796 (3) Å and O10···O10($\frac{1}{4}-y$, $\frac{1}{4}+x$, $-\frac{3}{4}-z$) 2.816 (3) Å.

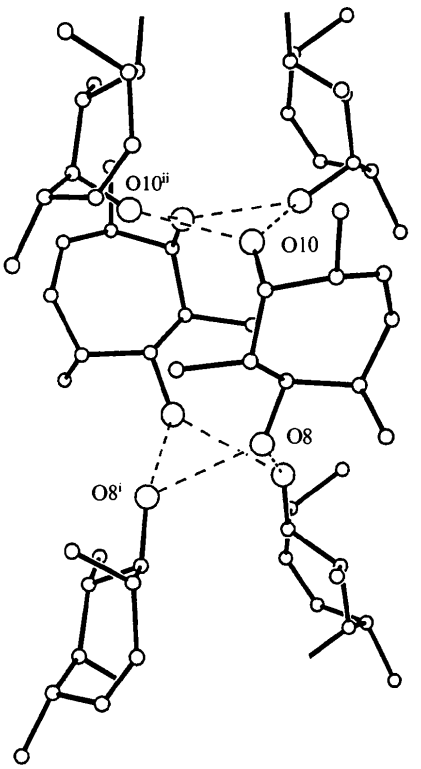


Fig. 2. A view of the title molecules illustrating the hydrogen-bonding scheme; the dashed lines show intermolecular O···O hydrogen-bonded contacts. O and C atoms are shown as open spheres and H atoms have been omitted.

Experimental

Pale yellow crystals of the title compound were obtained as shown in the scheme above and were recrystallized at 278 K from pentane–ethyl acetate solution (1:1) over seven days.

Crystal data

$C_{10}H_{18}O_2$
M_r = 170.24
Tetragonal
$I4_1/a$
a = 19.942 (3) Å
c = 10.294 (2) Å
V = 4093.8 (12) Å^3
Z = 16
D_x = 1.105 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 19.8–28.6°
μ = 0.075 mm^{-1}
T = 293 (2) K
Needle
0.31 × 0.20 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1922 measured reflections
1805 independent reflections
817 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0281
θ_{max} = 25.01°
h = 0 → 23
k = 0 → 23
l = 0 → 12
3 standard reflections
frequency: 120 min
intensity decay: <3.1%

Refinement

Refinement on F^2
$R(F)$ = 0.040
$wR(F^2)$ = 0.109
S = 1.102
1804 reflections
181 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.4222P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.028
$\Delta\rho_{max}$ = 0.122 e Å^{-3}
$\Delta\rho_{min}$ = −0.133 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.06949 (14)	0.33383 (13)	−0.0670 (3)	0.0500 (7)
C2	0.13200 (13)	0.30374 (13)	−0.1279 (2)	0.0441 (7)
C3	0.14072 (13)	0.31994 (13)	−0.2723 (2)	0.0425 (7)
C4	0.15499 (13)	0.39298 (13)	−0.3044 (3)	0.0495 (7)
C5	0.09359 (15)	0.43613 (13)	−0.2934 (3)	0.0549 (8)
C6	0.0552 (2)	0.44308 (14)	−0.1905 (3)	0.0606 (8)
C7	0.0644 (2)	0.41034 (13)	−0.0600 (3)	0.0602 (8)
O8	0.06675 (12)	0.30813 (10)	0.0639 (2)	0.0693 (7)
C9	0.1346 (2)	0.2283 (2)	−0.1089 (3)	0.0626 (9)
O10	0.08475 (9)	0.29930 (10)	−0.3492 (2)	0.0493 (5)
C11	0.1882 (2)	0.3994 (2)	−0.4377 (4)	0.0714 (10)
C12	0.1212 (3)	0.4426 (2)	0.0172 (4)	0.0882 (12)

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

C1—O8	1.442 (3)	C3—C4	1.520 (3)
C1—C2	1.519 (3)	C4—C5	1.501 (4)
C1—C7	1.531 (3)	C4—C11	1.529 (4)
C2—C9	1.519 (4)	C5—C6	1.314 (4)
C2—C3	1.531 (3)	C6—C7	1.505 (4)
C3—O10	1.429 (3)	C7—C12	1.527 (5)
O8—C1—C2	106.0 (2)	C5—C4—C3	112.3 (2)
O8—C1—C7	107.9 (2)	C5—C4—C11	111.9 (3)
C2—C1—C7	117.9 (2)	C3—C4—C11	110.9 (2)
C9—C2—C1	111.5 (2)	C6—C5—C4	126.6 (3)
C9—C2—C3	109.3 (2)	C5—C6—C7	127.1 (3)
C1—C2—C3	114.3 (2)	C6—C7—C12	111.9 (3)
O10—C3—C4	107.6 (2)	C6—C7—C1	113.5 (2)
O10—C3—C2	112.8 (2)	C12—C7—C1	113.3 (3)
C4—C3—C2	115.7 (2)		

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8···O8^i	0.80 (3)	2.01 (3)	2.796 (3)	165 (3)
O10—H10···O10^{ii}	0.83 (3)	2.03 (3)	2.816 (3)	158 (3)

Symmetry codes: (i) $\frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (ii) $\frac{1}{4} - y, \frac{1}{4} + x, -\frac{3}{4} - z$.

The space group was determined uniquely from the Laue symmetry and by the conditions limiting possible reflections; hkl present if $h + k + l = 2n$, $hk0$ present if $h,(k) = 2n$, $00l$ present if $l = 4n$. H atoms were refined with isotropic displacement parameters and C—H bond lengths are in the range 0.88 (3)–1.04 (3) Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XCAD-4 Software* (Siemens, 1993). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

This research was supported by NSERC Canada, the A. P. Sloan Foundation, the Merck Frosst Centre for Therapeutic Research, Eli Lilly Grantee Program, Bio-Mega and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles have been deposited with the IUCr (Reference: FG1032). 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 5.0. Enraf–Nonius, Delft, The Netherlands.

Lautens, M., Abd-El-Aziz, A. & Lough, A. (1990). *J. Org. Chem.* **55**, 5305.

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

Siemens (1993). *XCAD-4 Software. Program to Extract Intensity Data from Enraf–Nonius CAD-4 Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1995). C**51**, 914–916

Fortesyl 2-Phenylpropionate. An Example of a Novel Hydrocarbon Skeleton Containing Three Fused Five-Membered Rings

A. Gil Fortes, Robert A. W. Johnstone and David Whittaker

Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, England

Norman J. Lewis

SmithKline Beecham Pharmaceuticals, Leigh, Tonbridge, Kent TN11 9AN, England

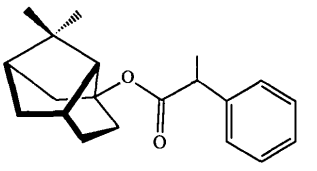
(*Received* 22 *March* 1994; *accepted* 2 *November* 1994)

Abstract

The title compound is 8,8-dimethyltricyclo[4.2.1.$0^{3,7}$]-nonan-6-yl 2-phenylpropionate, $C_{20}H_{26}O_2$. Fortesol (8,8-dimethyltricyclo[4,2,1,$0^{3,7}$]nonan-6-ol), derived by acid-catalysed rearrangement of nopyl tosylate, is chiral and forms diastereoisomeric esters with enantiomeric carboxylic and phosphonic acids.

Comment

Fortesol was prepared by Giddings, Jones-Parry, Owen & Whittaker (1986) after solvolysis of the tosylate of a known terpenoid, nopol, in acetic acid. The title compound, (I), was prepared recently by Fortes, Johnstone, Lewis & Whittaker (1994) by reacting chiral fortesol† with racemic 2-phenylpropionyl chloride. The X-ray spectrum of one of the diastereoisomers of the resulting fortesyl 2-phenylpropionate has revealed that the structure previously reported for fortesol by Giddings, Jones-Parry, Owen & Whittaker (1986) was completely erroneous. Fortesol has three fused five-membered rings rather than the previously suggested structure with one six-membered and two four-membered rings.



(I)

Although there are many fused multi-ring hydrocarbons, particularly among terpenes and their derivatives, it is believed that the newly discovered structure of the hydrocarbon skeleton of fortesol is unique. A similar system having a six-membered and two five-membered fused rings has been described by Corey & Glass (1967). The mechanism of rearrangement of nopyl tosylate in acetic acid to give fortesyl acetate has been discussed elsewhere (Fortes, Johnstone, Lewis & Whittaker, 1994).

† The IUPAC name assigned to fortesol in the paper by Fortes, Johnstone, Lewis & Whittaker (1994) was incorrect with respect to the numbering system.

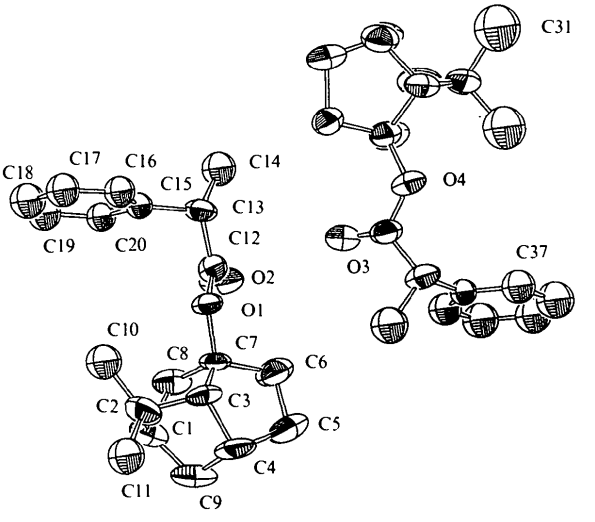


Fig. 1. Two identical molecules of fortesyl 2-phenylpropionate in the unit cell (with 50% probability ellipsoids and H atoms omitted for clarity).