N(22)—H(22)···O(211^{iii})	2.36 (3)	2.938 (3)	123 (2)
N(312)—H(322)···O(531^{iv})	2.18 (3)	3.006 (3)	159 (3)
N(22)—H(22)···O(521^{iv})	2.39 (3)	3.193 (3)	151 (3)
N(312)—H(322)···O(131^{v})	2.75 (3)	3.242 (3)	117 (3)
C(41)—H(41)···O(121^{ii})	2.61 (2)	3.353 (3)	138 (2)
Adduct (2)			
O(111)—H(111)···O(211)	1.57 (6)	2.452 (5)	169 (6)
N(22)—H(22)···O(211)	1.90 (5)	2.709 (5)	149 (5)
N(22)—H(22)···O(311)	2.21 (5)	2.882 (4)	131 (4)
N(312)—H(312)···O(311)	2.43 (7)	3.036 (7)	131 (6)
N(312)—H(311)···N(12^{vi})	2.26 (6)	3.036 (7)	152 (5)
N(42)—H(42)···O(101^{vii})	1.58 (8)	2.745 (6)	155 (7)
N(42)—H(42)···O(111^{vii})	2.27 (8)	3.295 (6)	138 (5)
C(52)—H(52)···O(511^{viii})	2.40 (7)	3.089 (7)	126 (5)
C(52)—H(52)···O(511^{ix})	2.66 (7)	3.172 (7)	112 (5)

Symmetry codes: (i) $x, y, z-1$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (iii) $x, y, 1+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, 2-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, 1+z$; (vi) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (vii) $\frac{3}{2}-x, y-\frac{3}{2}, \frac{1}{2}+z$; (viii) $x-\frac{1}{2}, -\frac{1}{2}-y, z$; (ix) $x-\frac{1}{2}, \frac{1}{2}-y, z$.

The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares (*SHELXL*93; Sheldrick, 1993) with anisotropic displacement parameters for all non-H atoms. H atoms were located by difference methods.

For both compounds, data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992); molecular graphics: *PLATON*92 (Spek, 1990).

The authors acknowledge financial assistance from the Australian Research Council, The University of Queensland and the Centre for Instrumental and Developmental Chemistry of the Queensland University of Technology.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Byriel, K. A., Kennard, C. H. L., Lynch, D. E., Smith, G. & Thompson, J. G. (1992). *Aust. J. Chem.* **45**, 969–981.

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

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual.* Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Hindawey, A. M., Nasser, A. M. G., Issa, R. M. & Issa, Y. M. (1980). *Indian J. Chem.* **19**A, 615–619.

Issa, Y. M., Hindawey, A. M., El-Kholy, A. E. & Issa, R. M. (1981). *Gazz. Chim. Ital.* **111**, 27–33.

Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1992). *Acta Cryst.* C**48**, 1265–1267.

Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1994). *Acta Cryst.* C**50**, 1291–1294.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Smith, G., Lynch, D. E., Byriel, D. A. & Kennard, C. H. L. (1995*a*). *Acta Cryst.* C**51**, 2629–2633.

Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995*b*). *Aust. J. Chem.* **48**, 1133–1149.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Sundaralingam, M. & Jensen, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.

Acta Cryst. (1996). C**52**, 235–237

5-*O*-Acetylcuauhtemonyl 6-*O*-2′,3′-Epoxy-2′-methylbutyrate

Ahmed A. Ahmed,[a] Basma A. Ali,[a] Mariusz Krawiec[b] and William H. Watson[b]

[a]*Department of Chemistry, Faculty of Science, El-Minia University, El-Minia 61519, Egypt, and* [b]*Department of Chemistry, Texas Christian University, Fort Worth TX 76129, USA*

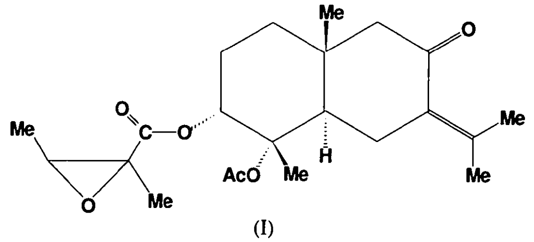
(*Received 4 April 1995; accepted 29 September 1995*)

Abstract

The title compound, $C_{22}H_{32}O_6$, is a sesquiterpene isolated from *Pluchea carolinensis* (*Compositae*). The X-ray structure is consistent with a compound isolated from other species of *Pluchea* and elucidated from spectroscopic data [Nakanishi, Crouch, Miura, Dominguez, Zamudio & Villarreal (1974). *J. Am. Chem. Soc.* **96**, 609–611].

Comment

As a part of our chemical study of the terpenoid constituents of *Compositae* plants, we investigated the CH_2Cl_2 extract of *Pluchea carolinensis*, (I). The genus *Pluchea* (tribe *Inuleae*, family *Compositae*) is traditionally placed in the subtribe *Plucheinae*. Several species of the genus have been studied chemically and it was shown that eudesmane derivatives are typical components (Ahmad, Farooqui, Sultana, Fizza & Khatoon, 1992; Uchiyama, Miyase, Ueno & Usmanghani, 1991; Ahmad, Farooqui, Fizza, Sultana & Khatoon, 1992; Ahmad, Fizza & Amber, 1989). Some *Pluchea* species are known for their medical properties (Mukhopadhyay *et al.*, 1983).



(I)

The two cyclohexane rings are *trans* fused, with both methyl groups (at C4 and C10) being axial (*cis* to one another). The acetoxy group is equatorial and located *cis* relative to the bulky axial (2,3-epoxy-2-methylbutyroyloxy) group. The methyl groups on the oxirane ring (at C19 and C20) are *trans* to one another. The dihedral angle between the oxirane ring and the carboxyl group (O5, C18, O4, C3) is 65.5 (7)°.

The torsion angle O4—C3—C4—O2 is −37.5 (7)° (*versus* −45.9° in cuauhtemone) which indicates a

©1996 International Union of Crystallography
Printed in Great Britain – all rights reserved

significant twist of the two ester groups around C3—C4 from its ideal arrangement ($\tau = -60°$).

The conjugated system of double bonds, O1═C8—C7═C11, is not planar [torsion angle −39 (1)°], but is less twisted than in cuauhtemone ($\tau = -46°$). All C—C and C—O bond distances, as well as intra-annular torsion angles, in the molecule do not differ significantly from the corresponding distances and torsion angles in the unsubstituted cuauhtemone (Ivie, Watson & Dominguez, 1974).

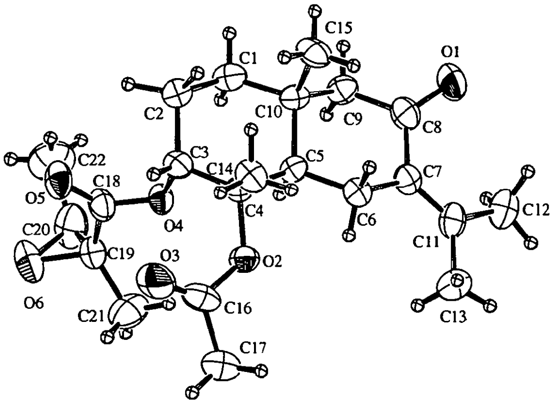


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids, except for those of H atoms which are of arbitrary size.

Experimental

The CH_2Cl_2 extract of the aerial parts of *Pluchea carolinensis* has been separated on a silica gel column to afford the cuauhtemone derivative.

Crystal data

$C_{22}H_{32}O_6$
$M_r = 392.49$
Monoclinic
$P2_1$
$a = 6.5104\,(18)$ Å
$b = 12.812\,(3)$ Å
$c = 13.480\,(2)$ Å
$\beta = 98.09\,(2)°$
$V = 1113.2\,(4)$ Å^3
$Z = 2$
$D_x = 1.171$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 36.74$–$39.57°$
$\mu = 0.69$ mm^{-1}
$T = 295$ K
Parallelepiped
0.40 × 0.40 × 0.15 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.853$, $T_{\max} = 1.000$
4802 measured reflections
2416 independent reflections

1339 observed reflections [$I \geq 4\sigma(I)$]
$R_{\rm int} = 0.063$
$\theta_{\max} = 79.40°$
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 150 reflections
intensity decay: −0.5%

Refinement

Refinement on F
$R = 0.0666$
$wR = 0.0631$
$S = 3.210$
1339 reflections
252 parameters
$w = 1/\sigma^2(F_{\rm obs})$
$(\Delta/\sigma)_{\max} = 0.020$

$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O1	0.714 (1)	−0.2521	0.5356 (5)	8.1 (4)
O2	0.5249 (8)	0.1715 (4)	0.7260 (4)	5.1 (2)
O3	0.346 (1)	0.2781 (6)	0.8162 (7)	9.3 (5)
O4	0.6369 (8)	0.0913 (5)	0.9074 (4)	4.9 (2)
O5	0.525 (1)	0.1248 (5)	1.0536 (5)	6.8 (3)
O6	0.908 (1)	0.2123 (5)	1.1264 (5)	8.0 (3)
C1	0.541 (1)	−0.1287 (6)	0.8497 (7)	6.1 (4)
C2	0.395 (2)	−0.0543 (6)	0.8944 (6)	6.5 (5)
C3	0.432 (1)	0.0585 (5)	0.8618 (6)	4.8 (3)
C4	0.416 (1)	0.0743 (6)	0.7514 (5)	4.5 (3)
C5	0.552 (1)	−0.0070 (6)	0.7034 (5)	4.3 (3)
C6	0.542 (1)	0.0040 (6)	0.5897 (6)	5.4 (3)
C7	0.692 (1)	−0.0655 (6)	0.5472 (6)	5.1 (3)
C8	0.702 (1)	−0.1765 (5)	0.5882 (6)	5.7 (4)
C9	0.695 (1)	−0.1854 (6)	0.6969 (6)	5.6 (4)
C10	0.522 (1)	−0.1227 (6)	0.7346 (6)	4.8 (3)
C11	0.806 (1)	−0.0359 (7)	0.4768 (6)	5.7 (4)
C12	0.958 (2)	−0.1041 (7)	0.4325 (7)	7.2 (5)
C13	0.797 (2)	0.0721 (7)	0.4380 (8)	8.2 (6)
C14	0.193 (1)	0.0827 (6)	0 6978 (6)	6.1 (4)
C15	0.311 (1)	−0.1719 (6)	0.6892 (7)	6.7 (4)
C16	0.466 (2)	0.2650 (6)	0.7607 (8)	6.7 (5)
C17	0.593 (2)	0.3485 (7)	0.7175 (8)	7.5 (5)
C18	0.655 (1)	0.1255 (6)	0.9984 (6)	5.7 (4)
C19	0.875 (1)	0.1739 (7)	1.0271 (6)	5.9 (4)
C20	1.008 (2)	0.1181 (9)	1.0993 (8)	8.4 (6)
C21	0.948 (2)	0.2434 (8)	0.9549 (8)	8.4 (5)
C22	0.957 (2)	0.0243 (8)	1.155 (1)	11.1 (9)

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

O1—C8	1.209 (8)	C5—C6	1.53 (1)
O2—C4	1.497 (8)	C5—C10	1.561 (8)
O2—C16	1.36 (1)	C6—C7	1.50 (1)
O3—C16	1.17 (1)	C7—C8	1.52 (1)
O4—C3	1.449 (9)	C7—C11	1.34 (1)
O4—C18	1.293 (9)	C8—C9	1.48 (1)
O5—C18	1.20 (1)	C9—C10	1.53 (1)
O6—C19	1.414 (9)	C10—C15	1.55 (1)
O6—C20	1.44 (1)	C11—C12	1.51 (1)
C1—C2	1.53 (1)	C11—C13	1.48 (1)
C1—C10	1.54 (1)	C16—C17	1.52 (1)
C2—C3	1.540 (9)	C18—C19	1.56 (1)
C3—C4	1.49 (1)	C19—C20	1.40 (1)
C4—C5	1.56 (1)	C19—C21	1.45 (1)
C4—C14	1.53 (1)	C20—C22	1.48 (2)
C4—O2—C16	119.4 (7)	C1—C10—C5	108.8 (5)
C3—O4—C18	117.1 (6)	C1—C10—C9	110.3 (6)
C19—O6—C20	58.9 (6)	C1—C10—C15	108.7 (7)
C2—C1—C10	113.4 (6)	C5—C10—C9	106.4 (6)
C1—C2—C3	109.8 (7)	C5—C10—C15	114.6 (6)
O4—C3—C2	108.9 (6)	C9—C10—C15	108.0 (6)
O4—C3—C4	108.4 (6)	C7—C11—C12	125.3 (7)
C2—C3—C4	114.9 (6)	C7—C11—C13	121.4 (8)
O2—C4—C3	111.8 (5)	C12—C11—C13	113.3 (8)
O2—C4—C5	98.4 (6)	O2—C16—O3	126.2 (8)
O2—C4—C14	106.3 (5)	O2—C16—C17	107 (1)
C3—C4—C5	111.0 (5)	O3—C16—C17	126.5 (8)

C3—C4—C14	114.2 (7)	O4—C18—O5	127.3 (9)
C5—C4—C14	113.9 (6)	O4—C18—C19	109.1 (7)
C4—C5—C6	113.9 (5)	O5—C18—C19	123.5 (7)
C4—C5—C10	114.9 (6)	O6—C19—C18	112.7 (7)
C6—C5—C10	111.6 (5)	O6—C19—C20	61.5 (6)
C5—C6—C7	113.0 (6)	O6—C19—C21	113.6 (7)
C6—C7—C8	114.4 (7)	C18—C19—C20	115.1 (8)
C6—C7—C11	124.0 (7)	C18—C19—C21	117.1 (7)
C8—C7—C11	121.5 (7)	C20—C19—C21	123 (1)
O1—C8—C7	122.5 (8)	O6—C20—C19	59.6 (5)
O1—C8—C9	122.3 (7)	O6—C20—C22	114 (1)
C7—C8—C9	115.2 (6)	C19—C20—C22	127 (1)
C8—C9—C10	114.4 (6)		

O1—C8—C7—C6	139.2 (9)	C3—C2—C1—C10	−56.7 (9)
O1—C8—C7—C11	−39 (1)	C3—C4—O2—C16	−58.5 (8)
O1—C8—C9—C10	−131.2 (8)	C3—C4—C5—C6	179.6 (6)
O2—C4—C3—O4	−37.5 (7)	C3—C4—C5—C10	49.1 (8)
O2—C4—C3—C2	−159.6 (6)	C4—O2—C16—C17	−176.2 (7)
O2—C4—C5—C6	−63.0 (6)	C4—C3—O4—C18	151.4 (6)
O2—C4—C5—C10	166.4 (5)	C4—C5—C6—C7	172.9 (6)
O3—C16—O2—C4	6 (1)	C4—C5—C10—C9	−169.2 (6)
O4—C3—C2—C1	−66.9 (9)	C4—C5—C10—C15	71.5 (8)
O4—C3—C4—C5	71.3 (6)	C5—C4—O2—C16	−175.2 (6)
O4—C3—C4—C14	−158.3 (5)	C5—C6—C7—C8	43.9 (9)
O4—C18—C19—O6	−179.3 (6)	C5—C6—C7—C11	−138.1 (8)
O4—C18—C19—C20	−111.3 (8)	C5—C10—C9—C8	−56.7 (8)
O4—C18—C19—C21	46 (1)	C6—C5—C4—C14	49.1 (8)
O5—C18—O4—C3	7 (1)	C6—C5—C10—C9	59.1 (8)
O5—C18—C19—O6	3 (1)	C6—C5—C10—C15	−60.2 (9)
O5—C18—C19—C20	71 (1)	C6—C7—C8—C9	−41 (1)
O5—C18—C19—C21	−132 (1)	C6—C7—C11—C12	180.0 (7)
O6—C19—C20—C22	99 (1)	C6—C7—C11—C13	3 (1)
O6—C20—C19—C18	−103.3 (9)	C7—C6—C5—C10	−54.9 (9)
O6—C20—C19—C21	101 (1)	C7—C8—C9—C10	49 (1)
C1—C2—C3—C4	55 (1)	C8—C7—C11—C12	−2 (1)
C1—C10—C5—C4	−50.4 (8)	C8—C7—C11—C13	−179.4 (8)
C1—C10—C5—C6	177.9 (6)	C8—C9—C10—C15	66.8 (8)
C1—C10—C9—C8	−174.6 (6)	C9—C8—C7—C11	140.9 (8)
C2—C1—C10—C5	54.5 (9)	C10—C5—C4—C14	−81.5 (7)
C2—C1—C10—C9	170.9 (6)	C14—C4—O2—C16	66.7 (8)
C2—C1—C10—C15	−70.9 (8)	C18—C19—O6—C20	107.3 (9)
C2—C3—O4—C18	−83.0 (7)	C18—C19—C20—C22	−5 (1)
C2—C3—C4—C5	−50.8 (9)	C19—O6—C20—C22	−121 (1)
C2—C3—C4—C14	79.6 (8)	C20—O6—C19—C21	−117 (1)
C3—O4—C18—C19	−170.5 (6)	C21—C19—C20—C22	−161 (1)

All non-H atoms were refined with anisotropic displacement parameters. H atoms were included in the difference Fourier map locations or at calculated positions with isotropic displacement parameters estimated from the displacement parameter of the adjacent C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*; *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *LS TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PLATON* (Spek, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahmad, V. U., Farooqui, T. A., Fizza, K., Sultana, A. & Khatoon, R. (1992). *J. Nat. Prod.* **55**, 730–735.

Ahmad, V. U., Farooqui, T. A., Sultana, A., Fizza, K. & Khatoon, R. (1992). *Phytochemistry*, **31**, 2888–2890.

Ahmad, V. U., Fizza, K. & Amber, A.-Ur-R. (1989). *J. Nat. Prod.* **52**, 861–863.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46,

Ivie, R. A., Watson, W. H. & Dominguez, X. A. (1974). *Acta Cryst.* B**30**, 2891–2893.

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

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, S. & Clegg,W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.

Mukhopadhyay, S., Cordell, G. A., Ruangrungsi, N., Rodkird, S., Tantivatana, P. & Hylands, P. J. (1983). *J. Nat. Prod.* **46**, 671–674.

Nakanishi, K., Crouch, R., Miura, I., Dominguez, X. A., Zamudio, A. & Villarreal, R. (1974). *J. Am. Chem. Soc.* **96**, 609–611.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34

Uchiyama, T., Miyase, T., Ueno, A. & Usmanghani, K. (1991). *Phytochemistry*, **30**, 655–657.

©1996 International Union of Crystallography
Printed in Great Britain – all rights reserved

Acta Cryst. (1996). C**52**, 237–244

Structural Aspects of the Nucleophilic Attack of Ketone Enolate on Dehydrodihydropyran

Sandra Ianelli,[a] Mario Nardelli,[a]* Daniele Belletti,[a] Brigitte Jamart-Grégoire,[b] Sophie Mercier-Girardot[b] and Paul Caubère[b]

[a]*Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy, and* [b]*Laboratoire de Chimie Organique I, UA CNRS No. 457, Université de Nancy I, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France*

(Received 21 December 1994; accepted 24 July 1995)

Abstract

The results of the crystal structure analyses of (6*RS*,7*SR*,8*RS*)-7-methyl-8-phenyl-3-oxabicyclo[4.2.0]oct-1-en-8-ol ($C_{14}H_{16}O_2$), (1*SR*,2*RS*,8*RS*)-8-methylthio-3-oxatricyclo[6.4.0.0^{2,7}]dodec-6-en-1-ol ($C_{12}H_{18}O_2S$) and (1*RS*,2*RS*,6*SR*,7*SR*,8*RS*)-8-methyl-3-oxatricyclo[6.4.0.0^{2,7}]dodeca-1,6,7-triol ($C_{12}H_{20}O_4$) allow interpretation of the nucleophilic attack reactions of ketone enolates on the short-lived dehydrodihydropyran intermediate, showing

Acta Crystallographica Section C
ISSN 0108-2701 ©1996