2132 reflections
212 parameters
All H atoms refined
$w = 1/(\sigma_F^2)^2$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Scattering factors from Stewart, Davidson & Simpson (1965) for H and Cromer & Waber (1974) for C and O atoms

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

O1—C10	1.282 (3)	C1—C7	1.513 (3)
O2—C10	1.228 (3)	C3—C8	1.502 (3)
O3—C11	1.296 (2)	C5—C9	1.507 (3)
O4—C11	1.222 (3)	C7—C10	1.499 (3)
O5—C12	1.298 (3)	C8—C11	1.502 (3)
O6—C12	1.216 (3)	C9—C12	1.506 (3)
C10—O1—H10	114 (2)	O2—C10—C7	121.8 (2)
C11—O3—H11	111 (2)	O3—C11—O4	123.8 (2)
C12—O5—H12	108 (2)	O3—C11—C8	113.3 (2)
C1—C7—C10	108.6 (2)	O4—C11—C8	123.0 (2)
C3—C8—C11	115.3 (2)	O5—C12—O6	123.1 (2)
C5—C9—C12	113.6 (2)	O5—C12—C9	114.0 (2)
O1—C10—O2	122.7 (2)	O6—C12—C9	122.9 (2)
O1—C10—C7	115.5 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H10···O4^{i}	1.06 (4)	1.61 (4)	2.670 (2)	178 (3)
O1—H10···O5^{ii}	1.06 (4)	2.88 (3)	3.020 (2)	87 (2)
O3—H11···O2^{iii}	1.02 (3)	1.64 (3)	2.650 (2)	172 (3)
O5—H12···O6^{iv}	1.05 (4)	1.64 (4)	2.692 (2)	178 (3)
O5—H12···O1^{ii}	1.05 (4)	2.88 (3)	3.020 (2)	87 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iii) $1+x, y, z$; (iv) $1-x, -1-y, 1-z$.

The Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group $P2_1/n$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1266). Services for accessing these data are described at the back of the journal.

References

Bell, W., Coupar, P. I., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 2520–2524.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Duchamp, D. J. & Marsh, R. E. (1967). *Acta Cryst.* B**25**, 5–19.
Fitzgerald, L. J. & Gerkin, R. E. (1993). *Acta Cryst.* C**49**, 1952–1958.
Fitzgerald, L. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 1838–1841.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

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Intermediates in the Synthesis of Forskolin. I

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Abstract

In 4-acetyl-3,4-epoxy-3,6,6,8b-tetramethyl-2a,3,4,6,7,8,8a,8b-octahydro-2*H*-naphtho[1,8a,8-*bc*]furan-2-one, $C_{17}H_{22}O_4$, the saturated ring (*A*) adopts a chair conformation, the cyclohexene ring (*B*) a distorted half-chair conformation and the furan ring an envelope conformation. The lactone and the epoxy moieties are *trans* to each other.

Comment

Forskolin, (3), is a polyoxygenated labdanyl diterpenoid isolated from the root of *Coleus forskohlii* Briq. (Bhat, Bajwa, Dornauer & de Souza, 1977). This natural

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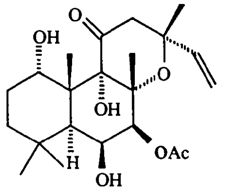
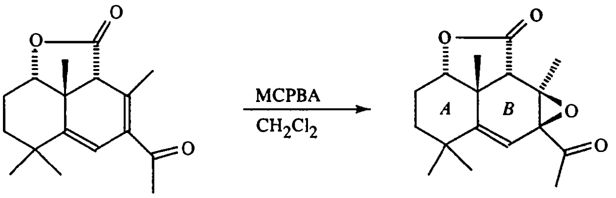
product has been seen as a potential drug to treat glaucoma and asthma (Bhat *et al.*, 1983). The synthesis of this compound has been a challenge for chemists, not only because of its biological interest but also its structural characteristics such as the presence of the tetrahydropyran-2-one group bonded to the *trans*-decalin moiety and the existence of eight chiral centres, seven of which are contiguous. To the best of our knowledge, only three complete syntheses of (±)-forskolin have been described (Ziegler, Jaynes & Saidane, 1987; Corey, Jardine & Rohloff, 1988; Hashimoto, Sakata, Sonegawa & Ikegami, 1988).



(3)

As the success of a synthetic route depends on the generation of intermediates with the correct functionality and stereochemistry, the unambiguous determination of the intermediates is required. We report here the crystal structure determination of one of them, (1).



(2) (1)

Compound (1) was obtained from a diene, (2), *via* an unusual regioselective epoxidation route (Malvestiti, 1994). The epoxidation of a diene, with one of its double bonds conjugated to a carbonyl group is, in general, regioselective. Under the conditions of the present study, we expected that the non-conjugated double bond would be oxidized (March, 1992); however, this was not the case.

A *ZORTEP* (Zsolnai, 1994) illustration of the formula unit is presented in Fig. 1. Cremer & Pople's (1975) puckering parameters show that ring *A* is in a chair conformation [q_2 = 0.091 (3), q_3 = 0.479 (3), Q = 0.487 (3) Å; θ = 10.6 (4), φ = 82.0 (19)°] with C7 and C8b lying at distances of −0.626 (3) and 0.516 (3) Å, respectively, from the least-squares plane through C8, C8a, C8c, C6; ring *B* is in a distorted half-chair conformation [q_2 = 0.397 (3), q_3 = −0.147 (3), Q = 0.423 (3) Å; θ = 110.4 (4), φ = 147.0 (4)°]. The furan ring adopts an envelope conformation [q_2 = 0.398 (3) Å, φ_2 = 107.0 (4)°] with atom C8b occupying the flap position, at a distance of 0.624 (3) Å from the least-squares plane made up of the remaining four atoms in the ring. The molecules are joined through C—H···O interactions: C2a···O3^{i} = 3.353 (3), HC2a···O3^{i} = 2.32 Å, C2a—HC2a···O3^{i} = 161°; C9···O4^{ii} = 3.360 (4), HC9*B*···O4^{ii} = 2.84 Å, C9—HC9*B*···O4^{ii} = 116° [symmetry operations (i) = 0.5 + x, 0.5 − y, z; (ii) = 0.5 − x, 0.5 + y, − z].

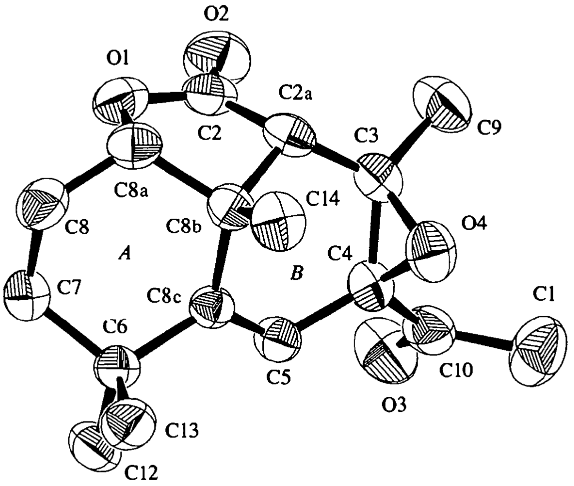


Fig. 1. The molecular structure of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

A possible explanation for this unexpected epoxidation route may be that, in compound (2), the two double bonds in ring *B* are twisted to each other and the acetyl moiety is also twisted out of the plane of ring *B* (Aboud, Malvestiti, Boldea, Walker & Battiste, 1995), so that the double bond is not totally conjugated to the carbonyl group.

Experimental

The crystals were obtained by slow evaporation from hexane/Et_2O at 269 K.

Crystal data

$C_{17}H_{22}O_4$
M_r = 290.36
Monoclinic
$P2_1/a$
a = 13.943 (2) Å
b = 8.0371 (7) Å
c = 14.3740 (10) Å
β = 108.030 (10)°
V = 1531.7 (3) Å^3
Z = 4
D_x = 1.2591 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.20–16.17°
μ = 0.089 mm^{-1}
T = 293 (2) K
Prismatic
0.50 × 0.45 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2823 measured reflections
2698 independent reflections
1821 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0106$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 16$
2 standard reflections
frequency: 60 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.111$
$S = 1.065$
2698 reflections
191 parameters
H-atom coordinates fixed, one common U
$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2 + 0.9295P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.197$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.194$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C2	1.349 (3)	O4—C4	1.457 (3)
O1—C8a	1.469 (3)	C2—C2a	1.516 (4)
O2—C2	1.197 (3)	C3—C4	1.469 (3)
O3—C10	1.208 (3)	C5—C8c	1.329 (3)
O4—C3	1.446 (3)		
C2—O1—C8a	109.7 (2)	O4—C4—C5	117.0 (2)
C3—O4—C4	60.81 (15)	C3—C4—C5	118.2 (2)
O4—C3—C4	59.93 (15)	O4—C4—C10	114.1 (2)
O4—C3—C9	115.5 (2)	C3—C4—C10	120.7 (2)
C4—C3—C9	123.5 (2)	C5—C4—C10	115.4 (2)
O4—C3—C2a	112.5 (2)	C5—C8c—C6	121.7 (2)
C4—C3—C2a	114.4 (2)	C5—C8c—C8b	119.0 (2)
C9—C3—C2a	117.2 (2)	C6—C8c—C8b	119.2 (2)
O4—C4—C3	59.26 (15)		

The H atoms were found from difference Fourier maps and included as fixed contributors. Only an overall isotropic displacement parameter was refined and converged to U = 0.075 (2) Å^2.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1275). Services for accessing these data are described at the back of the journal.

References

Abboud, K. A., Malvestiti, I., Boldea, L., Walker, M. A. & Battiste, M. A. (1995). *Acta Cryst.* **C51**, 995–997.

Bhat, S. V., Bajwa, B. S., Dornauer, H. & de Souza, N. J. (1977). *Tetrahedron Lett.* **19**, 1669–1672.

Bhat, S. V., Dohadwalla, A. N., Bajwa, B. S., Dadkar, N. K., Dornauer, H. & de Souza, N. J. (1983). *J. Med. Chem.* **26**, 486–492.

Corey, E. J., Jardine, P. S. & Rohloff, J. C. (1988). *J. Am. Chem. Soc.* **110**, 3672–3673.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

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

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

Hashimoto, S., Sakata, S., Sonegawa, M. & Ikegami, S. (1988). *J. Am. Chem. Soc.* **110**, 3670–3672.

Malvestiti, I. (1994). PhD thesis, Departamento de Química, Universidade Federal de São Carlos, Brazil.

March, J. (1992). *Advanced Organic Chemistry: Reaction and Mechanism and Structure*, 4th ed., pp. 826–827. London: John Wiley.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

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

Ziegler, F. E., Jaynes, B. H. & Saidane, M. T. (1987). *J. Am. Chem. Soc.* **109**, 8115–8116.

Zsolnai, L. (1994). *ZORTEP. Interactive Graphics Program*. University of Heidelberg, Germany.

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N-(2-Pyridinium)urea Perchlorate[†]

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Abstract

The *N*-(2-pyridinium)urea cation of the title compound, $C_6H_8N_3O^+.ClO_4^-$, is planar within 0.022 (2) Å and adopts an *s-cis-s-cis* conformation with respect to the imino C—N bonds. The structure consists of centrosymmetric dimers of cations ordered in layers parallel to the ($\bar{1}03$) plane, and hydrogen-bonded anions.

Comment

This article is part of a project investigating adducts of urea derivatives and inorganic salts unsymmetrically substituted by π-conjugated substituents as potential non-linear materials. The adduct of *N*-(2-pyridyl)urea (2pU) with $HReO_4$ was found to crystallize in the centrosymmetric space group $P\bar{1}$ (Velikova, Petrova & Angelova, 1997) and contain cationic hydrogen-bonded dimers. Here we changed the counter ion to a tetrahedral but smaller ClO_4^- anion in order to investigate its effect on the cationic geometry and arrangement.

[†] Alternative name: 2-ureidopyridinium perchlorate.