Chalcone epoxide intermediates in the syntheses of lignin-related phenyl-coumarans

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Compounds (2R*,3S*)-1-(3,4-dimethoxyphenyl)-3-{3-methoxy-2-[(2R*)-tetrahydropyran-2-yloxy]phenyl}-2,3-epoxy-1-propanone, $C_{23}H_{26}O_7$, (I), and trans-1-(3,4-dimethoxyphenyl)-3-[3-methoxy-2-(methoxymethoxy)phenyl]-2,3-epoxy-1-propan-one, $C_{20}H_{22}O_7$, (II), were obtained on epoxidation of chalcones. The stereochemistries of (I) and (II) were elucidated. In both compounds, the substituents on the oxirane ring are trans-oriented. Compound (I) was obtained together with a diastereometric form that differs from (I) with respect to the configuration of the asymmetric C atom in the tetrahydropyran group. The geometries of the substituted oxirane rings of (I) and (II) are very similar. The hydrogen-bonding patterns, mediated via weak C—H⋯O interactions, differ considerably. The crystal structures of (I) and (II) are compared with those of related chalcone epoxides. The conversion of (I) and (II) into lignin-related phenylcoumarans is discussed.

Comment

Compounds (I) and (II) are obtained on epoxidation of chalcones (Li & Lundquist, 1997). Compound (I) (m.p. 401 K) and a diastereomer (m.p. 370–371 K) are obtained on epoxidation of the chalcone 1-(3,4-dimethoxyphenyl)-3-[3-methoxy-2-(tetrahydropyran-2-yloxy)phenyl]prop-2-en-1-one. The epoxidation is accomplished with hydrogen peroxide using a method involving phase-transfer catalysis (Brunow & Lundquist, 1981, 1984). The epoxides can be converted to a lignin model of the phenylcoumaran type, (III), in three reaction steps, viz. BF_3-catalysed rearrangement, sodium borohydride reduction and acid-catalysed ring closure. The yield of (III) obtained from (II) was low (Li & Lundquist, 1997). Studies of the reactions involved have shown that the outcome of the rearrangement reaction is strongly dependent on the structure of the epoxide and the conditions prevailing during the reaction (Ralph et al., 1987; Li et al., 1993). It should be noted that

reduction of the rearrangement product with sodium borohydride under alkaline conditions lowers the yield substantially (Li et al., 1993). The synthesis of the cis isomer
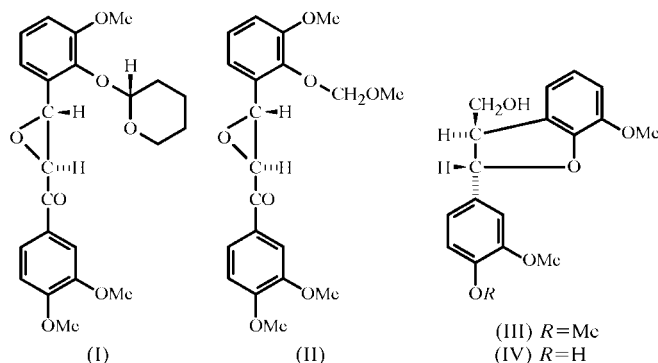
corresponding to (III) using (I) as starting material has been described (Li et al., 1997). The lignin model (IV) has also been prepared via a chalcone epoxide (Brunow & Lundquist, 1984); the stereochemistry of (IV) has been established by a crystal structure determination (Stomberg & Lundquist, 1987). Compound (IV) has been used as starting material in the synthesis of neolignans of the phenylcoumaran type (Juhász et al., 2000, 2001). It is notable that a chalcone epoxide of the topical type is an intermediate in the synthesis of the flavonolignan silychristin (Tanaka et al., 1989).

Perspective drawings and the atom numbering of (I) and (II) are shown in Figs. 1 and 2, respectively. Selected bond distances and angles for both compounds are given in Table 3. The crystal structures establish the stereochemistries of (I) and (II), and confirm their molecular structures. It can be concluded from comparison of the ^{1}H NMR spectra (Li & Lundquist, 1997) of (I) and its diastereomer of melting point 370–371 K with those of the trans (Matano, 1994) and cis forms (Kumar & Bhakuni, 1996) of 1,3-diphenyl-2,3-epoxy-1-propanone that the diastereomers differ with respect to the
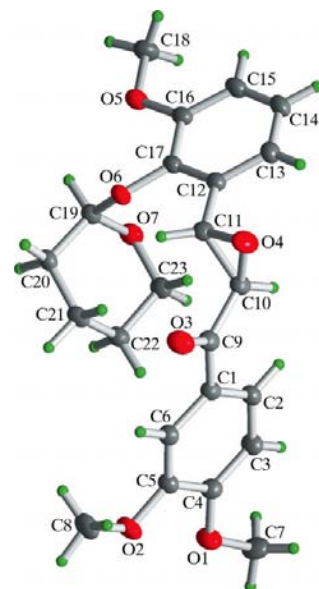

Figure 1
A perspective drawing of (I), showing the atom numbering. The atomic displacement ellipsoids are shown at the 50% probability level.

configuration of the asymmetric C atom in the tetrahydro-pyran group. The substituents on the oxirane rings of (I) and (II) are *trans*-oriented. Chalcone epoxides described in the literature in general have the *trans* configuration, but chalcone epoxides with the *cis* configuration are known (Wasserman & Aubrey, 1955; Matano, 1994; Kumar & Bhakuni, 1996).

Except for the C10—C11 and O4—C11 bond lengths and angles involving the atoms of the oxirane rings (the C9—C10—C11 angles differ by 2.1°), the bond lengths and angles in the central parts of (I) and (II) are, within experimental error, the same (Table 3). The C1—C9—C10—C11 and C9—C10—C11—C12 torsion angles (denoted τ_2 and τ_3 in Table 4) differ just slightly, by 0.8 and 0.6°, respectively.

Comparison with the crystal structures of related chalcone epoxides was performed after a search of the Cambridge Structural Database (CSD; Version 5.27 of November 2005, plus two updates; Allen, 2002). The substituents on the oxirane ring are *trans*-oriented in the chalcone epoxides subjected to crystal structure determinations to date. Some pertinent structural data are tabulated in Table 4. It is apparent that torsion angle τ_3 is less flexible than torsion angle τ_2. The angles between the planes of the aromatic rings differ considerably.

There are weak C—H···O hydrogen bonds present in the crystal structures of both (I) and (II). (For geometrical details and notations of these hydrogen bonds see Tables 1 and 2.) The hydrogen-bonding patterns of (I) and (II) are quite different. For (I), on the first-level graph set, defined by Bernstein *et al.* (1995) and Grell *et al.* (1999), the following chains are formed: $C(4)$ by hydrogen bond *a*, $C(5)$ by *f*, $C(6)$ by *b*, $C(8)$ by *d*, and $C(10)$ by *c* and *e*. On the second-level graph set, $R_2^2(10)$ (*a*, *b*), $R_2^2(27)$ (*a*, *f*) and $R_2^2(29)$ (*b*, *f*) rings, and $C_1^2(8)$ (*d*, *e*), $C_2^2(8)$ (*a*, *b*), $C_2^2(10)$ (*a*, *c*; *b*, *c*), $C_2^2(14)$ (*a*, *c*), $C_2^2(15)$ (*c*, *d*), $C_2^2(16)$ (*b*, *c*), $C_2^2(17)$ (*c*, *e*), $C_2^2(18)$ (*a*, *d*; *c*, *d*; *d*, *e*), $C_2^2(19)$ (*d*, *f*; *e*, *f*), $C_2^2(20)$ (*a*, *e*; *b*, *d*; *c*, *e*), $C_2^2(22)$ (*b*, *e*), $C_2^2(24)$
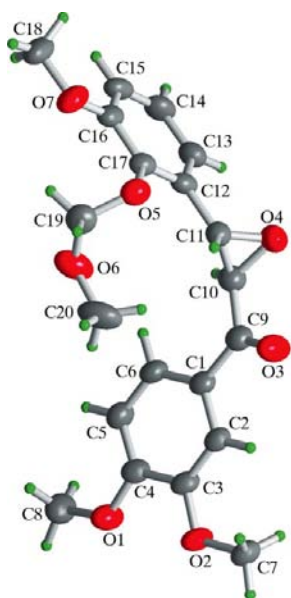
(c, f) and $C_2^2(29)$ (b, f) chains were recognized. For (II), the hydrogen bonds can be described just on the first graph-set level, *viz.* a $C(8)$ chain for *a*, and intramolecular strings $S(5)$ for *b* and $S(6)$ for *c*. The assignments of graph-set descriptors were performed using *PLUTO*, as described by Motherwell *et al.* (1999). All the examined chalcone epoxides (Table 4) have different hydrogen-bonding patterns.

Experimental

The syntheses of compounds (I) and (II) were described by Li & Lundquist (1997). Crystals of (I) (m.p. 401 K) and (II) (m.p. 381–382 K) were obtained from ethanol.

Compound (I)

Crystal data

$C_{23}H_{26}O_7$	$Z = 4$
$M_r = 414.44$	$D_x = 1.365$ Mg m^{-3}
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 14.4281$ (5) Å	$\mu = 0.10$ mm^{-1}
$b = 18.8386$ (7) Å	$T = 173$ (2) K
$c = 9.0887$ (3) Å	Prism, colourless
$\beta = 125.285$ (1)°	$0.42 \times 0.22 \times 0.18$ mm
$V = 2016.52$ (12) Å^3	

Data collection

Siemens SMART CCD area-detector diffractometer	18037 measured reflections
	3639 independent reflections
ω scans	3193 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$R_{int} = 0.034$
$T_{min} = 0.608$, $T_{max} = 0.982$	$\theta_{max} = 33.2°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.072P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 0.020P]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
3639 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
274 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

Label	D—H···A	D—H	H···A	D···A	D—H···A
a	C3—H3···O1^i	0.95	2.56	3.415 (2)	150
b	C7—H7A···O2^i	0.98	2.48	3.396 (2)	155
c	C7—H7B···O4^{ii}	0.98	2.53	3.456 (2)	157
d	C14—H14···O3^{iii}	0.95	2.56	3.458 (2)	158
e	C18—H18A···O3^{iv}	0.98	2.45	3.384 (2)	158
f	C21—H21A···O7^v	0.99	2.59	3.2139 (19)	121

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

Compound (II)

Crystal data

|	
$C_{20}H_{22}O_7$	$Z = 4$
$M_r = 374.38$	$D_x = 1.345$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.7503$ (10) Å	$\mu = 0.10$ mm^{-1}
$b = 9.4201$ (7) Å	$T = 173$ (2) K
$c = 15.4409$ (12) Å	Needle with an arrowhead end, colourless
$\beta = 94.706$ (2)°	
$V = 1848.3$ (2) Å^3	$0.65 \times 0.14 \times 0.06$ mm

Figure 2
A perspective drawing of (II), showing the atom numbering. The atomic displacement ellipsoids are shown at the 50% probability level.

Data collection

Siemens SMART CCD area-detector diffractometer	19850 measured reflections
ω scans	3280 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	2257 reflections with $I > 2\sigma(I)$
	$R_{\mathrm{int}} = 0.057$
$T_{\min} = 0.805$, $T_{\max} = 0.994$	$\theta_{\max} = 25.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_{\mathrm{o}}^2) + (0.0524P)^2 + 0.460P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_{\mathrm{o}}^2 + 2F_{\mathrm{c}}^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.01$	$\Delta\rho_{\max} = 0.39$ e Å^{-3}
3280 reflections	$\Delta\rho_{\min} = -0.14$ e Å^{-3}
270 parameters	
H-atom parameters constrained	

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

Label	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
a	C7—H7C$\cdots$O3$^{\mathrm{i}}$	0.98	2.53	2.923 (3)	104
b	C11—H11$\cdots$O5	1.00	2.40	2.788 (3)	102
c	C19—H19B$\cdots$O7	0.99	2.29	2.924 (3)	121

Symmetry code: (i) $-x + 2$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$.

Table 3
Selected geometrical parameters (Å, °) for compounds (I) and (II).

Bond	(I)	(II)	Angle	(I)	(II)
C1—C9	1.483 (2)	1.478 (3)	C1—C9—C10	118.37 (13)	118.46 (19)
O3—C9	1.215 (2)	1.211 (2)	O3—C9—C1	122.03 (14)	121.7 (2)
C9—C10	1.504 (2)	1.502 (3)	O3—C9—C10	119.47 (14)	119.9 (2)
C10—C11	1.489 (2)	1.473 (3)	O4—C10—C9	115.59 (13)	116.10 (18)
O4—C10	1.4256 (19)	1.426 (3)	O4—C10—C11	58.99 (10)	58.57 (13)
O4—C11	1.4359 (19)	1.418 (3)	O4—C11—C10	58.31 (10)	59.07 (13)
C11—C12	1.483 (2)	1.483 (3)	C10—O4—C11	62.71 (10)	62.36 (13)
			O4—C11—C12	117.26 (13)	118.07 (18)
			C9—C10—C11	115.84 (14)	117.93 (19)
			C10—C11—C12	121.84 (14)	122.35 (19)

Table 4
Comparative geometrical parameters (°) for examined chalcone epoxides.

Code	τ_1	τ_2	τ_3	A/B
(I)^a	147	123.41 (15)	−149.91 (13)	85.44 (9)
(II)^a	148	122.6 (2)	−149.3 (2)	89.92 (10)
EXEWOT^b	157	122.8	−154.2	107.7
EXEWOT^c	149	101.5	−151.1	65.3
FATQOH^{d*}	147	113.0	−154.2	48.6
LIGXUU^e	169 (5)	112.8 (7)	−151.0 (6)	99.0
LIGXUU01^f	157 (15)	145 (1)	−149 (1)	114.5
QECFAF^g	148	147.4	−150.5	127.3
QINFIC^h	151	143.3	−150.7	144.0
SOMHEH^i	106	119.9	−148.4	93.9
WAMLOM^j	148	121.5	−152.1	87.1
TECTAX^k	147	158.8	−153.2	133.1
VAZBOO^{l*}	150	150.0	−154.6	103.8

Notes: $\tau_1 = $ H10—C10—C11—H11, $\tau_2 = $ C1—C9—C10—C11, $\tau_3 = $ C9—C10—C11—C12 and A/B is the angle between the aromatic rings in relation to the oxirane group. References: (*a*) this work; (*b*) Bakó *et al.* (2004), first molecule; (*c*) Bakó *et al.* (2004), second molecule; (*d*) Shi *et al.* (2004); (*e*) Stomberg *et al.* (1994), monoclinic form; (*f*) Stomberg *et al.* (1994), trigonal form; (*g*) Bakó *et al.* (1999); (*h*) Bardet *et al.* (1999); (*i*) Baures *et al.* (1990); (*j*) Xu *et al.* (2005); (*k*) Zhang *et al.* (2006); (*l*) Cuthbertson *et al.* (2005); (*) racemic crystal – data for the opposite enantiomer are deposited in the CSD.

H atoms were allowed for isotropically and constrained to ideal geometry using an appropriate riding model. For methyl groups, the C—H distances (0.98 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on the threefold averaged circular Fourier synthesis. For other H atoms, C—H distances were set at 0.95–1.00 Å. For (I), U_{iso}(H) values were fixed at 1.2 or 1.5 times U_{eq}(C).

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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