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(2*R*,3a*S*,5a*R*,8a*R*,8b*S*)-4-Bromo-2-(4-methoxyphenyl)-7,7-dimethyl-3a,5a,-8a,8b-tetrahydrobenzo[1,2-*d*:3,4-*d*′]-bis[1,3]dioxole

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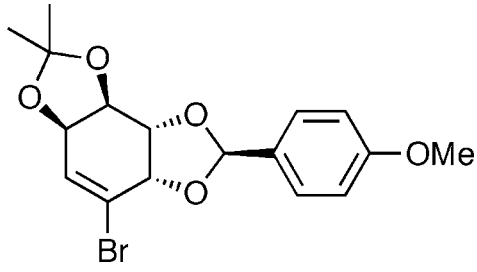
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; R factor = 0.034; wR factor = 0.078; data-to-parameter ratio = 13.9.

The title compound, $C_{17}H_{19}BrO_5$, bears an *exo*-orientated or *R*-configured 4-methoxyphenyl group and incorporates a C—O bond that is distinctly shorter than the three remaining acetal C—O bonds [1.415 (4) *versus* 1.431 (4)–1.448 (4) Å and 1.421 (4) *versus* 1.436 (4)–1.448 (4) Å for the two molecules in the asymmetric unit].

Related literature

For related literature, see: Banwell *et al.* (2003); Boyd *et al.* (1991); Hulme *et al.* (2005).



Experimental

Crystal data

$C_{17}H_{19}BrO_5$
M_r = 383.24
Monoclinic, $P2_1$
a = 5.2285 (1) Å
b = 33.4467 (9) Å
c = 9.4726 (3) Å
β = 91.7226 (12)°
V = 1655.78 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.51 mm^{-1}
T = 200 K
0.45 × 0.14 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: integration *via* Gaussian method (Coppens, 1970) implemented in *maXus* (Mackay *et al.*, 1999)
T_{min} = 0.546, T_{max} = 0.892
20604 measured reflections
5796 independent reflections
4970 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.078
S = 0.97
5796 reflections
416 parameters
1 restraint
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}
Absolute structure: Flack (1983), 2828 Friedel pairs
Flack parameter: −0.012 (6)

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEPII* (Johnson, 1976) in *TEXSAN* (Molecular Structure Corporation, 1997); software used to prepare material for publication: *CRYSTALS*.

We thank the Australian Research Council for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2471).

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supplementary materials

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(2*R*,3a*S*,5a*R*,8a*R*,8b*S*)-4-Bromo-2-(4-methoxyphenyl)-7,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[1,2-*d*:3,4-*d*']bis[1,3\]dioxole

M. G. Banwell, O. J. Kokas and A. C. Willis

Comment

As part of a program directed towards exploiting microbially derived and enantiomerically pure *cis*-1,2-dihydrocatechols in the synthesis of certain biologically active natural products (Banwell *et al.*, 2003), we generated an epimeric mixture of compounds (I) and (II) then subjected this to reaction with DIBAL-H. At 195–233 K one of these two benzylidene acetals participated more readily in the anticipated reductive cleavage reaction leading to the desired *p*-methoxybenzyl ether (III). The unreacted epimer was recovered and subjected to single-crystal X-ray analysis and thus establishing that it was compound (II) incorporating an *exo*-orientated or *R*-configured 4-methoxyphenyl group at C2. This outcome is consistent with the notion that the reactive epimer (I) can, by virtue of reduced steric effects, complex DIBAL-H at the O1-acetal oxygen more readily than (II) and thus engage, selectively, in the ring-cleavage process leading to target (III). The present structure represents only the second reported for a 4-methoxyphenylacetal derivative of a *cis*-cyclohexane-1,2-diol (Hulme *et al.*, 2005).

The crystallographic asymmetric unit within the solid-state structure of compound (II) consists of two independent molecules. The compound is enantiomerically pure and its absolute configuration has been determined by refinement of the Flack parameter. The outcome of this determination is in agreement with that predicted on the basis of the absolute configuration of the precursor, *viz.* (1*S*,2*S*)-3-bromo-3,5-cyclohexadiene-1,2-diol (Boyd *et al.*, 1991). The three non-aromatic rings within the title compound are each close to planar and with the two 1,3-dioxolane rings clearly attached to the opposite faces of the central cyclohexene residue. The allylic and homo-allylic C–O bonds associated with the two heterocyclic rings are all of similar length (1.430–1.438 Å) but the C2–O3 bond is notably shorter than the three remaining acetal carbon to oxygen bonds (1.418 *vs* 1.438–1.444 Å) within the molecule. The origins of this variation are unclear at the present time.

Experimental

A magnetically stirred solution of a 5:3 mixture of the benzylidene acetals (I) and (II) (88 mg, 0.23 mmol) in anhydrous dichloromethane/pentane (1.4 ml of a 1:1 *v*/*v* mixture) was cooled to 195 K then treated, dropwise, with DIBAL-H (1.15 ml of a 1.0 *M* solution in dichloromethane). The resulting mixture was warmed to 233 K and after 6 h at this temperature was treated with sodium potassium tartrate (5 ml of a 1 *M* aqueous solution). The ensuing mixture was allowed to stir at 291 K for 2 h then the separated aqueous fraction was extracted with dichloromethane (3 × 40 ml). The combined organic phases were washed with brine (1 × 50 ml) then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a clear, colourless oil. Subjection of this material to flash chromatography (silica, 1:4 *v*/*v* ethyl acetate/hexane elution) afforded two fractions, A and B.

Concentration of fraction A (R_f = 1/5) under reduced pressure afforded the benzyl ether (III) [41 mg, 74% based on available (I)] as a clear, colourless oil, $[\alpha]_D$ −59.9 (*c* 0.05, $CHCl_3$) (Found: $M^{+\cdot}$, 384.0570. $C_{17}H_{21}{}^{79}BrO_5$ requires $M^{+\cdot}$, 384.0572). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (2*H*, d, *J* = 8.7 Hz), 6.90 (2*H*, d, *J* = 8.7 Hz), 6.24 (1*H*, d, *J* = 3.6 Hz), 4.84

(1*H*, d, *J* = 10.8 Hz), 4.68–4.61 (2*H*, complex m), 4.36 (2*H*, m), 4.15–4.10 (2*H*, complex m), 3.81 (3*H*, s), 1.43 (3*H*, s), 1.36 (3*H*, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 130.1, 129.9, 128.6, 124.2, 114.1, 110.1, 77.9, 75.4, 74.0, 73.4, 70.5, 55.5, 28.1, 26.2 (one signal obscured or overlapping); ν_{max} (NaCl)/cm^{-1} 3460, 2924, 1612, 1516, 1464, 1254, 1089, 1046; MS (EI, 70 eV) 386 and 384 ($M^{+\cdot}$, both 3%), 256 (7), 137 (20), 121 (100), 101 (20), 81 (37), 69 (81), 55 (42), 43 (53).

Concentration of fraction B (R_f = 0.30) under reduced pressure afforded a solid that upon recrystallization (diethyl ether) gave the acetal (II) (30 mg, 90% recovery) as white plates, m.p. = 649–651 K, $[\alpha]_D$ = +49.4 (*c* 0.21, $CHCl_3$) [Found: (M – H·)$^+$, 381.0334. $C_{17}H_{19}{}^{79}BrO_5$ requires (M – H·)$^+$, 381.0338]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (2*H*, d, *J* = 8.4 Hz), 6.79 (2*H*, d, *J* = 8.4 Hz), 6.25 (1*H*, d, *J* = 3.6 Hz), 5.86 (1*H*, s), 4.91 (1*H*, d, *J* = 6.0 Hz), 4.64–4.60 (3*H*, complex m), 3.73 (3*H*, s), 1.40 (3*H*, s), 1.38 (3*H*, s); ν_{max} (NaCl)/cm^{-1} 2979, 2896, 1647, 1615, 1589, 1517, 1382, 1337, 1249, 1220, 1175, 1090, 1060, 1025, 948, 832; MS (EI, 70 eV) 384 and 382 ($M^{+\cdot}$, both 15%), 383 and 381 [(M – H·)$^+$, both 29], 336 and 334 (both 2), 200 (16), 161 (31), 137 (38), 136 (60), 135 (100), 108 (53), 77 (29), 43 (52).

Refinement

Hydrogen atoms were included at calculated positions and ride on the atoms to which they are bonded. The biggest features in a final difference electron density map are close to the Br atoms.

Figures

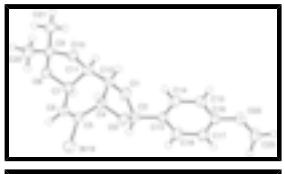


Figure 1. Anisotropic displacement ellipsoid plot of $C_{17}H_{19}BrO_5$ (molecule one) with labelling of selected atoms. Ellipsoids show 50% probability levels. Hydrogen atoms are drawn as circles with small radii.

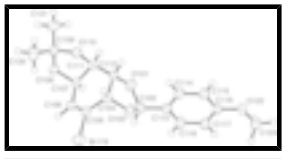
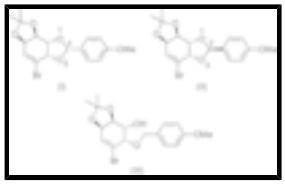


Figure 2. Anisotropic displacement ellipsoid plot of $C_{17}H_{19}BrO_5$ (molecule two) with labelling of selected atoms. Ellipsoids show 50% probability levels. Hydrogen atoms are drawn as circles with small radii.

Figure 3. Unit cell packing diagram of $C_{17}H_{19}BrO_5$ projected down the *a* axis. Hydrogen atoms are drawn as circles with small radii.



(2*R*,3a*S*,5a*R*,8a*R*,8 b*S*)- 4-Bromo-2-(4-methoxyphenyl)-7,7-dimethyl-3a,5a,8a,8 b-tetrahydrobenzo[1,2 – *d*:3,4 – *d*']bis[1,3]dioxole

Crystal data

$C_{17}H_{19}BrO_5$	F_{000} = 784

M_r = 383.24	D_x = 1.537 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 5.2285 (1) Å	Cell parameters from 55931 reflections
b = 33.4467 (9) Å	θ = 2.6–25º
c = 9.4726 (3) Å	μ = 2.51 mm^{-1}
β = 91.7226 (12)º	T = 200 K
V = 1655.78 (7) Å^3	Plate, colourless
Z = 4	0.45 × 0.14 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer	4970 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.038
T = 200 K	θ_{max} = 25.0º
φ and ω scans with CCD	θ_{min} = 2.8º
Absorption correction: integration via Gaussian method (Coppens, 1970) implemented in maXus (Mackay *et al.*, 1999)	h = −6→6
T_{min} = 0.546, T_{max} = 0.892	k = −39→39
20604 measured reflections	l = −11→11
5796 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.034	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.44P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$wR(F^2)$ = 0.078	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.97	$\Delta\rho_{max}$ = 0.58 e Å^{-3}
5796 reflections	$\Delta\rho_{min}$ = −0.82 e Å^{-3}
416 parameters	Extinction correction: None
1 restraint	Absolute structure: Flack (1983), 2828 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.012 (6)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.3464 (5)	0.40867 (9)	0.5958 (3)	0.0442
C2	0.2738 (7)	0.40850 (12)	0.7402 (4)	0.0359
O3	0.0221 (5)	0.39302 (8)	0.7424 (3)	0.0393
C4	−0.0224 (7)	0.37075 (11)	0.6148 (4)	0.0358
C5	0.0579 (8)	0.32792 (11)	0.6278 (4)	0.0382

C6	0.2260 (8)	0.30950 (12)	0.5503 (4)	0.0384
C7	0.3623 (7)	0.32944 (11)	0.4320 (4)	0.0345
O8	0.3249 (5)	0.30663 (8)	0.3051 (2)	0.0349
C9	0.1349 (7)	0.32616 (11)	0.2148 (4)	0.0348
O10	0.0409 (5)	0.35852 (8)	0.2978 (2)	0.0374
C11	0.2475 (7)	0.37002 (11)	0.3917 (4)	0.0364
C12	0.1353 (7)	0.39397 (12)	0.5098 (4)	0.0360
C13	0.2790 (7)	0.44947 (11)	0.8044 (4)	0.0333
C14	0.1061 (8)	0.47884 (12)	0.7616 (4)	0.0402
C15	0.1102 (8)	0.51620 (12)	0.8225 (4)	0.0408
C16	0.2883 (7)	0.52469 (11)	0.9305 (4)	0.0347
C17	0.4642 (8)	0.49634 (12)	0.9723 (4)	0.0422
C18	0.4595 (8)	0.45874 (12)	0.9093 (4)	0.0408
Br19	−0.11756 (10)	0.29887 (3)	0.76809 (4)	0.0609
C20	−0.0808 (7)	0.29762 (13)	0.1827 (4)	0.0448
C21	0.2636 (8)	0.34112 (13)	0.0852 (4)	0.0465
O22	0.2709 (5)	0.56229 (8)	0.9893 (3)	0.0439
C23	0.4571 (9)	0.57223 (12)	1.0977 (4)	0.0480
O101	0.8242 (5)	0.60404 (8)	0.6747 (3)	0.0444
C102	0.7448 (7)	0.60523 (11)	0.5282 (4)	0.0356
O103	0.4861 (5)	0.61825 (8)	0.5250 (3)	0.0392
C104	0.4501 (7)	0.64154 (11)	0.6503 (4)	0.0353
C105	0.5211 (7)	0.68426 (11)	0.6330 (4)	0.0337
C106	0.6957 (7)	0.70409 (11)	0.7083 (4)	0.0352
C107	0.8556 (7)	0.68488 (11)	0.8242 (4)	0.0325
O108	0.8519 (4)	0.70848 (9)	0.9508 (2)	0.0342
C109	0.6632 (7)	0.69170 (12)	1.0426 (4)	0.0358
O110	0.5563 (5)	0.65805 (8)	0.9668 (2)	0.0378
C111	0.7488 (8)	0.64532 (11)	0.8725 (4)	0.0363
C112	0.6229 (8)	0.61987 (12)	0.7581 (4)	0.0362
C113	0.7651 (7)	0.56493 (11)	0.4605 (4)	0.0323
C114	0.6019 (8)	0.53372 (12)	0.4985 (4)	0.0399
C115	0.6187 (8)	0.49680 (11)	0.4347 (4)	0.0388
C116	0.7973 (7)	0.49055 (11)	0.3318 (4)	0.0355
C117	0.9609 (8)	0.52082 (12)	0.2951 (4)	0.0414
C118	0.9423 (7)	0.55802 (12)	0.3611 (4)	0.0392
Br119	0.32031 (9)	0.71174 (3)	0.49172 (4)	0.0513
C120	0.4578 (8)	0.72146 (13)	1.0659 (5)	0.0527
C121	0.7960 (9)	0.67800 (14)	1.1778 (4)	0.0505
O122	0.7948 (6)	0.45324 (8)	0.2698 (3)	0.0429
C123	0.9839 (9)	0.44560 (13)	0.1674 (4)	0.0483
H21	0.3917	0.39055	0.7960	0.0430*
H41	−0.2078	0.37220	0.5861	0.0429*
H61	0.2651	0.28080	0.5711	0.0459*
H71	0.5489	0.33217	0.4563	0.0414*
H111	0.3748	0.38645	0.3405	0.0436*
H121	0.0332	0.41686	0.4701	0.0432*
H141	−0.0240	0.47275	0.6851	0.0480*
H151	−0.0141	0.53715	0.7893	0.0487*

H171	0.5957	0.50268	1.0478	0.0504*
H181	0.5880	0.43815	0.9403	0.0487*
H201	−0.0197	0.27581	0.1198	0.0536*
H202	−0.2251	0.31227	0.1341	0.0536*
H203	−0.1412	0.28577	0.2727	0.0536*
H211	0.1346	0.35471	0.0216	0.0560*
H212	0.4012	0.36053	0.1135	0.0560*
H213	0.3405	0.31807	0.0343	0.0560*
H231	0.4256	0.60002	1.1320	0.0576*
H232	0.6324	0.57057	1.0587	0.0576*
H233	0.4434	0.55302	1.1780	0.0576*
H1021	0.8522	0.62490	0.4770	0.0427*
H1041	0.2679	0.63956	0.6788	0.0424*
H1061	0.7226	0.73307	0.6875	0.0424*
H1071	1.0354	0.68137	0.7934	0.0391*
H1111	0.8841	0.62966	0.9249	0.0436*
H1121	0.5266	0.59745	0.8019	0.0436*
H1141	0.4723	0.53827	0.5723	0.0480*
H1151	0.5024	0.47460	0.4625	0.0465*
H1171	1.0916	0.51623	0.2219	0.0499*
H1181	1.0616	0.57999	0.3348	0.0472*
H1201	0.5305	0.74480	1.1196	0.0633*
H1202	0.3854	0.73078	0.9727	0.0633*
H1203	0.3194	0.70884	1.1213	0.0633*
H1211	0.6672	0.66636	1.2420	0.0606*
H1212	0.8821	0.70132	1.2252	0.0606*
H1213	0.9267	0.65726	1.1558	0.0606*
H1231	0.9627	0.41776	0.1303	0.0580*
H1232	0.9630	0.46507	0.0878	0.0580*
H1233	1.1584	0.44861	0.2123	0.0580*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0511 (17)	0.0465 (17)	0.0355 (14)	−0.0169 (13)	0.0087 (13)	−0.0127 (13)
C2	0.035 (2)	0.039 (2)	0.034 (2)	−0.0014 (17)	−0.0008 (16)	−0.0041 (17)
O3	0.0432 (16)	0.0415 (15)	0.0333 (14)	−0.0120 (13)	0.0064 (11)	−0.0104 (12)
C4	0.037 (2)	0.039 (2)	0.0318 (19)	−0.0038 (17)	−0.0044 (16)	−0.0093 (16)
C5	0.050 (3)	0.032 (2)	0.031 (2)	−0.0090 (18)	−0.0070 (18)	−0.0013 (17)
C6	0.051 (2)	0.032 (2)	0.032 (2)	0.0052 (17)	−0.0079 (17)	0.0006 (16)
C7	0.037 (2)	0.033 (2)	0.033 (2)	0.0052 (17)	−0.0006 (17)	−0.0070 (17)
O8	0.0360 (14)	0.0368 (16)	0.0312 (13)	0.0076 (11)	−0.0078 (11)	−0.0084 (11)
C9	0.037 (2)	0.036 (2)	0.032 (2)	0.0106 (16)	−0.0030 (16)	−0.0073 (16)
O10	0.0478 (15)	0.0364 (14)	0.0277 (13)	0.0114 (12)	−0.0035 (11)	−0.0080 (11)
C11	0.045 (2)	0.034 (2)	0.0309 (19)	−0.0037 (17)	0.0001 (16)	−0.0034 (16)
C12	0.050 (2)	0.030 (2)	0.0274 (19)	0.0009 (17)	−0.0008 (17)	−0.0041 (15)
C13	0.039 (2)	0.034 (2)	0.0274 (19)	−0.0039 (17)	0.0035 (16)	−0.0057 (16)
C14	0.044 (2)	0.042 (2)	0.034 (2)	0.0015 (19)	−0.0099 (18)	−0.0020 (18)

C15	0.050 (2)	0.034 (2)	0.038 (2)	0.0044 (18)	−0.0057 (18)	0.0018 (17)
C16	0.045 (2)	0.028 (2)	0.0310 (19)	−0.0050 (17)	0.0054 (16)	−0.0016 (15)
C17	0.044 (2)	0.040 (2)	0.042 (2)	0.0012 (19)	−0.0105 (18)	−0.0111 (18)
C18	0.044 (2)	0.037 (2)	0.041 (2)	0.0050 (18)	−0.0100 (18)	−0.0079 (17)
Br19	0.0886 (4)	0.0553 (3)	0.0393 (2)	−0.0281 (3)	0.0087 (2)	0.0010 (2)
C20	0.034 (2)	0.045 (2)	0.055 (2)	0.003 (2)	−0.0052 (17)	−0.015 (2)
C21	0.053 (3)	0.052 (3)	0.035 (2)	0.006 (2)	0.0036 (19)	−0.0011 (19)
O22	0.0618 (18)	0.0291 (15)	0.0407 (16)	−0.0040 (14)	−0.0010 (13)	−0.0046 (12)
C23	0.070 (3)	0.035 (2)	0.039 (2)	−0.018 (2)	−0.001 (2)	−0.0034 (18)
O101	0.0498 (17)	0.0489 (18)	0.0337 (14)	0.0165 (14)	−0.0081 (12)	−0.0132 (12)
C102	0.034 (2)	0.038 (2)	0.034 (2)	0.0044 (17)	−0.0005 (16)	−0.0067 (17)
O103	0.0385 (15)	0.0420 (15)	0.0367 (14)	0.0062 (12)	−0.0059 (11)	−0.0133 (12)
C104	0.038 (2)	0.035 (2)	0.033 (2)	0.0003 (17)	0.0032 (16)	−0.0087 (16)
C105	0.039 (2)	0.034 (2)	0.0290 (19)	0.0018 (17)	0.0033 (16)	−0.0022 (16)
C106	0.043 (2)	0.031 (2)	0.0314 (18)	−0.0011 (17)	0.0072 (16)	0.0014 (15)
C107	0.033 (2)	0.034 (2)	0.0303 (19)	0.0008 (16)	0.0020 (15)	−0.0057 (16)
O108	0.0395 (13)	0.0340 (14)	0.0293 (13)	−0.0040 (12)	0.0048 (10)	−0.0065 (13)
C109	0.037 (2)	0.039 (2)	0.0310 (19)	−0.0071 (17)	0.0038 (16)	−0.0057 (16)
O110	0.0482 (16)	0.0351 (15)	0.0305 (13)	−0.0101 (12)	0.0081 (12)	−0.0061 (11)
C111	0.047 (2)	0.031 (2)	0.031 (2)	0.0025 (17)	0.0043 (17)	−0.0026 (16)
C112	0.051 (2)	0.031 (2)	0.0268 (19)	−0.0019 (18)	0.0058 (17)	−0.0039 (15)
C113	0.036 (2)	0.032 (2)	0.0291 (18)	−0.0013 (17)	−0.0023 (16)	−0.0030 (16)
C114	0.047 (2)	0.040 (2)	0.033 (2)	−0.0009 (19)	0.0068 (18)	−0.0068 (17)
C115	0.046 (2)	0.036 (2)	0.035 (2)	−0.0040 (18)	0.0020 (18)	−0.0010 (17)
C116	0.044 (2)	0.029 (2)	0.033 (2)	0.0036 (17)	−0.0062 (17)	−0.0038 (16)
C117	0.044 (2)	0.043 (2)	0.038 (2)	−0.0008 (19)	0.0136 (18)	−0.0103 (18)
C118	0.040 (2)	0.035 (2)	0.043 (2)	−0.0019 (18)	0.0066 (18)	−0.0076 (18)
Br119	0.0586 (3)	0.0541 (3)	0.0406 (2)	0.0124 (2)	−0.00977 (18)	0.0001 (2)
C120	0.038 (2)	0.052 (3)	0.068 (3)	0.001 (2)	0.006 (2)	−0.016 (2)
C121	0.061 (3)	0.060 (3)	0.031 (2)	−0.009 (2)	−0.003 (2)	0.002 (2)
O122	0.0602 (19)	0.0300 (15)	0.0386 (16)	0.0026 (13)	0.0018 (13)	−0.0065 (12)
C123	0.067 (3)	0.041 (2)	0.037 (2)	0.018 (2)	0.001 (2)	−0.0042 (19)

Geometric parameters (Å, °)

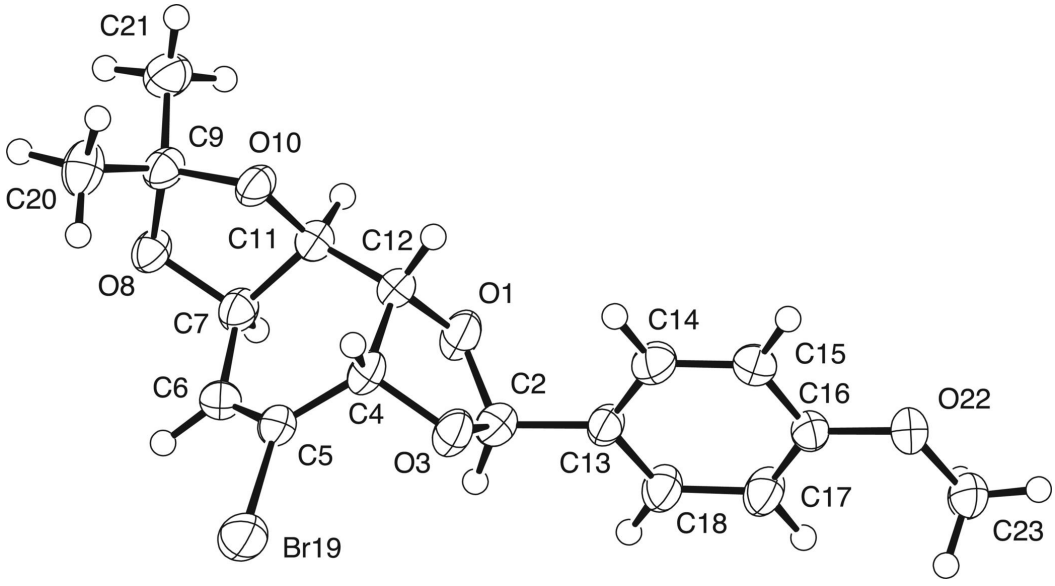
O1—C2	1.431 (4)	O101—C102	1.436 (4)
O1—C12	1.439 (4)	O101—C112	1.436 (4)
C2—O3	1.415 (4)	C102—O103	1.421 (4)
C2—C13	1.499 (5)	C102—C113	1.498 (5)
C2—H21	1.000	C102—H1021	1.000
O3—C4	1.433 (4)	O103—C104	1.437 (4)
C4—C5	1.497 (5)	C104—C105	1.486 (5)
C4—C12	1.524 (5)	C104—C112	1.527 (5)
C4—H41	1.000	C104—H1041	1.000
C5—C6	1.315 (5)	C105—C106	1.320 (5)
C5—Br19	1.904 (4)	C105—Br119	1.911 (4)
C6—C7	1.502 (6)	C106—C107	1.503 (5)
C6—H61	1.000	C106—H1061	1.000
C7—O8	1.432 (4)	C107—O108	1.436 (4)

C7—C11	1.528 (5)	C107—C111	1.513 (5)
C7—H71	1.000	C107—H1071	1.000
O8—C9	1.448 (4)	O108—C109	1.448 (4)
C9—O10	1.433 (4)	C109—O110	1.439 (4)
C9—C20	1.502 (5)	C109—C120	1.486 (6)
C9—C21	1.503 (5)	C109—C121	1.510 (5)
O10—C11	1.431 (4)	O110—C111	1.430 (4)
C11—C12	1.509 (5)	C111—C112	1.513 (5)
C11—H111	1.000	C111—H1111	1.000
C12—H121	1.000	C112—H1121	1.000
C13—C14	1.387 (5)	C113—C114	1.402 (5)
C13—C18	1.385 (5)	C113—C118	1.360 (5)
C14—C15	1.376 (6)	C114—C115	1.379 (5)
C14—H141	1.000	C114—H1141	1.000
C15—C16	1.391 (5)	C115—C116	1.386 (5)
C15—H151	1.000	C115—H1151	1.000
C16—C17	1.371 (5)	C116—C117	1.377 (5)
C16—O22	1.379 (4)	C116—O122	1.379 (4)
C17—C18	1.392 (5)	C117—C118	1.397 (5)
C17—H171	1.000	C117—H1171	1.000
C18—H181	1.000	C118—H1181	1.000
C20—H201	1.000	C120—H1201	1.000
C20—H202	1.000	C120—H1202	1.000
C20—H203	1.000	C120—H1203	1.000
C21—H211	1.000	C121—H1211	1.000
C21—H212	1.000	C121—H1212	1.000
C21—H213	1.000	C121—H1213	1.000
O22—C23	1.433 (4)	O122—C123	1.429 (5)
C23—H231	1.000	C123—H1231	1.000
C23—H232	1.000	C123—H1232	1.000
C23—H233	1.000	C123—H1233	1.000
C2—O1—C12	108.6 (3)	C102—O101—C112	109.0 (3)
O1—C2—O3	106.8 (3)	O101—C102—O103	106.1 (3)
O1—C2—C13	112.5 (3)	O101—C102—C113	111.5 (3)
O3—C2—C13	109.5 (3)	O103—C102—C113	110.3 (3)
O1—C2—H21	109.3	O101—C102—H1021	109.6
O3—C2—H21	109.3	O103—C102—H1021	109.6
C13—C2—H21	109.3	C113—C102—H1021	109.6
C2—O3—C4	107.8 (3)	C102—O103—C104	107.3 (3)
O3—C4—C5	113.0 (3)	O103—C104—C105	113.0 (3)
O3—C4—C12	102.1 (3)	O103—C104—C112	101.9 (3)
C5—C4—C12	112.7 (3)	C105—C104—C112	112.7 (3)
O3—C4—H41	109.6	O103—C104—H1041	109.7
C5—C4—H41	109.6	C105—C104—H1041	109.7
C12—C4—H41	109.6	C112—C104—H1041	109.7
C4—C5—C6	126.4 (4)	C104—C105—C106	126.5 (3)
C4—C5—Br19	113.9 (3)	C104—C105—Br119	113.9 (3)
C6—C5—Br19	119.7 (3)	C106—C105—Br119	119.5 (3)
C5—C6—C7	123.3 (3)	C105—C106—C107	122.7 (3)

C5—C6—H61	118.4	C105—C106—H1061	118.7
C7—C6—H61	118.4	C107—C106—H1061	118.7
C6—C7—O8	109.5 (3)	C106—C107—O108	110.7 (3)
C6—C7—C11	112.9 (3)	C106—C107—C111	113.1 (3)
O8—C7—C11	102.8 (3)	O108—C107—C111	102.3 (3)
C6—C7—H71	110.5	C106—C107—H1071	110.1
O8—C7—H71	110.5	O108—C107—H1071	110.1
C11—C7—H71	110.5	C111—C107—H1071	110.2
C7—O8—C9	109.2 (3)	C107—O108—C109	108.4 (3)
O8—C9—O10	104.9 (2)	O108—C109—O110	105.4 (3)
O8—C9—C20	109.3 (3)	O108—C109—C120	109.8 (3)
O10—C9—C20	108.9 (3)	O110—C109—C120	109.1 (3)
O8—C9—C21	108.5 (3)	O108—C109—C121	108.8 (3)
O10—C9—C21	111.4 (3)	O110—C109—C121	110.4 (3)
C20—C9—C21	113.4 (3)	C120—C109—C121	113.1 (4)
C9—O10—C11	106.2 (3)	C109—O110—C111	105.9 (3)
C7—C11—O10	101.5 (3)	C107—C111—O110	101.6 (3)
C7—C11—C12	116.5 (3)	C107—C111—C112	115.6 (3)
O10—C11—C12	107.5 (3)	O110—C111—C112	108.4 (3)
C7—C11—H111	110.3	C107—C111—H1111	110.3
O10—C11—H111	110.3	O110—C111—H1111	110.3
C12—C11—H111	110.3	C112—C111—H1111	110.3
C4—C12—C11	116.3 (3)	C104—C112—C111	116.6 (3)
C4—C12—O1	103.0 (3)	C104—C112—O101	103.6 (3)
C11—C12—O1	107.0 (3)	C111—C112—O101	106.9 (3)
C4—C12—H121	110.1	C104—C112—H1121	109.8
C11—C12—H121	110.1	C111—C112—H1121	109.8
O1—C12—H121	110.1	O101—C112—H1121	109.8
C2—C13—C14	121.7 (3)	C102—C113—C114	120.6 (3)
C2—C13—C18	119.9 (3)	C102—C113—C118	120.5 (3)
C14—C13—C18	118.4 (4)	C114—C113—C118	118.9 (3)
C13—C14—C15	121.3 (4)	C113—C114—C115	120.5 (4)
C13—C14—H141	119.4	C113—C114—H1141	119.8
C15—C14—H141	119.4	C115—C114—H1141	119.8
C14—C15—C16	119.7 (4)	C114—C115—C116	119.8 (4)
C14—C15—H151	120.2	C114—C115—H1151	120.1
C16—C15—H151	120.2	C116—C115—H1151	120.1
C15—C16—C17	119.9 (4)	C115—C116—C117	120.2 (4)
C15—C16—O22	115.6 (3)	C115—C116—O122	116.0 (3)
C17—C16—O22	124.5 (3)	C117—C116—O122	123.8 (3)
C16—C17—C18	119.9 (4)	C116—C117—C118	119.3 (4)
C16—C17—H171	120.1	C116—C117—H1171	120.3
C18—C17—H171	120.0	C118—C117—H1171	120.3
C17—C18—C13	120.8 (4)	C117—C118—C113	121.3 (4)
C17—C18—H181	119.6	C117—C118—H1181	119.4
C13—C18—H181	119.6	C113—C118—H1181	119.4
C9—C20—H201	109.5	C109—C120—H1201	109.5
C9—C20—H202	109.5	C109—C120—H1202	109.5
H201—C20—H202	109.5	H1201—C120—H1202	109.5

C9—C20—H203	109.5	C109—C120—H1203	109.5
H201—C20—H203	109.5	H1201—C120—H1203	109.5
H202—C20—H203	109.5	H1202—C120—H1203	109.5
C9—C21—H211	109.5	C109—C121—H1211	109.5
C9—C21—H212	109.5	C109—C121—H1212	109.5
H211—C21—H212	109.5	H1211—C121—H1212	109.5
C9—C21—H213	109.5	C109—C121—H1213	109.5
H211—C21—H213	109.5	H1211—C121—H1213	109.5
H212—C21—H213	109.5	H1212—C121—H1213	109.5
C16—O22—C23	116.7 (3)	C116—O122—C123	116.9 (3)
O22—C23—H231	109.5	O122—C123—H1231	109.5
O22—C23—H232	109.5	O122—C123—H1232	109.5
H231—C23—H232	109.5	H1231—C123—H1232	109.5
O22—C23—H233	109.5	O122—C123—H1233	109.5
H231—C23—H233	109.5	H1231—C123—H1233	109.5
H232—C23—H233	109.5	H1232—C123—H1233	109.5

Fig. 1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O10
C20
C11
C12
O8
O1
C7
C14
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C6
C2
C16
O22
C4
C5
O3
C13
C17
C18
C23
Br19

Fig. 2

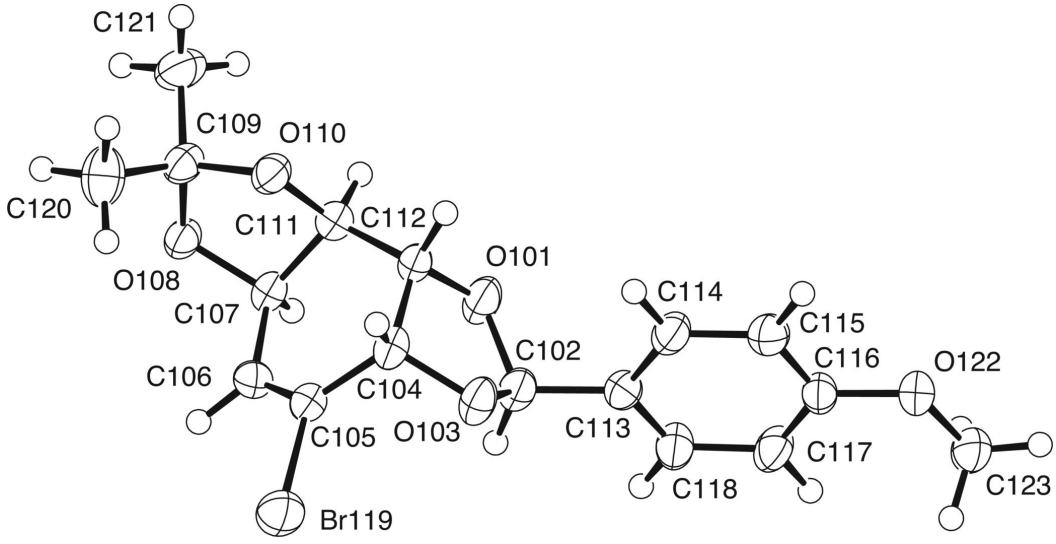
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Fig. 3

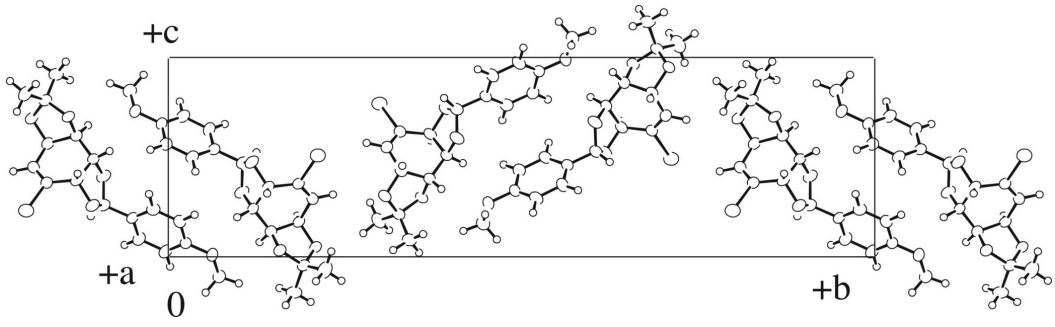

Fig. 4