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A cocrystal of (2*S*,3a*S*,4*R*,5*R*,7a*S*)- and (2*R*,3a*S*,4*R*,5*R*,7a*S*)-7-bromo-2-(4-methoxyphenyl)-3a,4,5,7a-tetrahydro-1,3-benzodioxole-4,5-diol (17:3)

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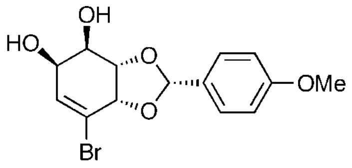
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.030; wR factor = 0.076; data-to-parameter ratio = 14.4.

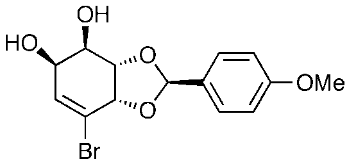
The title compounds, both $C_{14}H_{15}BrO_5$, cocrystallize and their structures, including absolute stereochemistries, have been solved simultaneously. The structures differ in the configuration (R *versus* S) at the acetal C atom bearing the 4-methoxyphenyl group.

Related literature

For related literature, see: Banwell *et al.* (2007*a*,*b*); Boyd *et al.* (1991); Hulme *et al.* (2005).



(major)



(minor)

Experimental

Crystal data

$C_{14}H_{15}BrO_5$
M_r = 343.17
Monoclinic, $P2_1$
a = 7.2245 (4) Å
b = 9.7093 (5) Å
c = 9.9373 (5) Å
β = 95.689 (3)°
V = 693.62 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.98 mm^{-1}
T = 200 K
0.40 × 0.29 × 0.26 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: integration via Gaussian method (Coppens, 1970) implemented in *maXus* (Mackay *et al.*, 1999)
T_{min} = 0.372, T_{max} = 0.586
12613 measured reflections
3108 independent reflections
2802 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.076
S = 0.99
3108 reflections
216 parameters
35 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}
Absolute structure: Flack (1983), with 1430 Friedel pairs
Flack parameter: −0.019 (10)

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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2294).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Banwell, M. G., Kokas, O. J. & Willis, A. C. (2007*a*). *Org. Lett.* **9**, 3503–3506.
Banwell, M. G., Kokas, O. J. & Willis, A. C. (2007*b*). *Acta Cryst.* E**63**, o3820.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Boyd, D. R., Dorrity, M. R. J., Hand, M. V., Malone, J. F., Sharma, N. D., Dalton, H., Gray, D. J. & Sheldrake, G. N. (1991). *J. Am. Chem. Soc.* **113**, 666–667.
Coppens, P. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hulme, A., Compton, T., Parsons, S. & Messenger, D. (2005). Private communication (refcode NASZAJ). CCDC, Union Road, Cambridge, England.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *maXus*. Nonius BV, Delft, The Netherlands, MacScience Co. Ltd, Japan, and University of Glasgow, Scotland.
Molecular Structure Corporation (1997). *TEXSAN*. Version 1.8. MSC, The Woodlands, Texas, USA.
Nonius (1997). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

supplementary materials

Acta Cryst. (2007). E**63**, o4187 [**doi:10.1107/S1600536807046995**]

A cocrystal of (2*S*,3a*S*,4*R*,5*R*,7a*S*)- and (2*R*,3a*S*,4*R*,5*R*,7a*S*)-7-bromo-2-(4-methoxyphenyl)-3a,4,5,7a-tetrahydro-1,3-benzodioxole-4,5-diol (17:3)

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

Comment

During the course of establishing a total synthesis of the non-natural enantiomeric form of the montanine alkaloid brunsvigine (Banwell *et al.*, 2007*a*) we had occasion to convert (1*S*,2*S*)-3-bromo-3,5-cyclohexadiene-1,2-diol (I) (Boyd *et al.*, 1991) into the corresponding 4-methoxybenzylidene acetal (II). This was achieved under standard conditions and provided compound (II) as a *ca* 5:3 mixture of epimers arising from a variation in stereochemistry at the newly installed acetal carbon. Subjection of this mixture to *cis*-dihydroxylation under the so-called UpJohn conditions resulted in each epimer reacting exclusively at the non-halogenated double bond and in a diastereofacially selective manner to give the corresponding mixture of *cis*-diols (III) and (IV) as a solid after recrystallization from ethyl acetate. In order to establish the relative stereochemistries within these two compounds a single-crystal X-ray analysis was undertaken. The present structures represent only the third and fourth reported for a 4-methoxyphenylacetal derivative of a *cis*-cyclohexane-1,2-diol (Banwell *et al.*, 2007*b*; Hulme *et al.*, 2005).

The crystallographic asymmetric unit consists of one molecule of $C_{14}H_{15}BrO_5$, but with some atoms disordered. The disordered atoms appear to indicate that two isomers have co-crystallized, with the atoms that are not disordered being common to both. The major epimer includes sites O18 and C10 to C19 (crystallographic labelling), and the minor epimer includes O118 and C110 to C119. The structures vary in configuration (*R versus S*) at the acetal carbon bearing the 4-methoxyphenyl group. The minor isomer atom sites have been refined with isotropic displacement parameters set equal to U_{eq} of the closest site of the major epimer. Restraints were applied to distances and angles of the minor sites so they would tend to match the corresponding values in the major epimer and so O118 and C110 to C117 would tend to be coplanar. The relative occupancies of the two isomers were refined.

The compounds are enantiomerically pure and their absolute configurations have been determined by refinement of the Flack parameter. The outcomes of these determinations are in agreement with those predicted on the basis of the absolute configuration of the precursor (I) (Boyd *et al.*, 1991).

The largest peaks in the final difference electron-density map are located near the Br atom and at the juncture between disordered and ordered parts of the structure(*s*).

Experimental

A magnetically stirred suspension of (1*S*,2*S*)-3-bromo-3,5-cyclohexadiene-1,2-diol (I) (20.0 g, 104.7 mmol) and 4-methoxybenzaldehyde dimethyl acetal (20.9 ml, 115.2 mmol) in anhydrous dichloromethane (200 ml) was cooled to 253 K then (1*S*)-(+)-camphor-10-sulfonic acid monohydrate (2.4 g, 10.4 mmol) was added. After 1 h the reaction mixture was quenched with sodium hydroxide (200 ml of a 1 *M* aqueous solution) and the separated aqueous phase extracted with dichloromethane (2 × 100 ml). The combined organic phases were washed with brine (1 × 100 ml) then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a white solid assumed to contain an epimeric mixture of the benzylidene acetals (II). A magnetically stirred solution of this material in acetone/water (300 ml of a 2:1 *v/v* mixture) was cooled to 273 K then treated with *N*-methylmorpholine *N*-oxide (27.1 g, 232 mmol) and osmium tetraoxide (7.0 ml of a 2.5% *w/v* solution in *tert*-butanol, 0.53 mmol). The ensuing mixture was stirred at 291 K for 20 h then treated with sodium metabisulfite (200 ml of a 20% *w/v* aqueous solution). After 4 h the reaction mixture was concentrated under reduced pressure to give a brown residue that was treated with diethyl ether (500 ml) then water (500 ml). The separated aqueous phase was extracted with diethyl ether (4 × 150 ml) and the combined organic fractions were then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a brown solid. Subjection of this material to flash chromatography (silica, 1:19 *v/v* methanol/dichloromethane elution) and concentration of the appropriate fractions ($R_f = 0.3$) afforded a *ca*. 4:1 mixture of the title compounds (III) and (IV) (23.3 g, 65%) as a white, crystalline solid, m.p. = 406–407 K [Found: $(M - H^\cdot)^+$, 384.0570. C, 48.67; H, 4.40; Br 23.42. $C_{14}H_{15}{}^{79}BrO_5$ requires $(M - H^\cdot)^+$, 384.0572. C, 49.00; H, 4.41; Br 23.28%]. ^{1}H NMR [300 MHz, $(CD_3)_2CO$] δ (major epimer) 7.42 (2*H*, d, *J* = 8.9 Hz), 6.95 (2*H*, d, *J* = 8.9 Hz), 6.29 (1*H*, m), 5.80 (1*H*, s), 4.90 (1*H*, d, *J* = 5.1 Hz), 4.55 (1*H*, m), 4.40 (3*H*, m), 4.25 (1*H*, m), 3.81 (3*H*, s); δ (minor epimer) 7.37 (2*H*, d, *J* = 8.7 Hz), 6.93 (2*H*, d, *J* = 8.7 Hz), 6.17 (1*H*, dd, *J* = 2.7 and 1.2 Hz), 5.87 (1*H*, s), 4.69 (1*H*, dd, *J* = 6.0 and 1.2 Hz), 4.51 (1*H*, t, *J* = 4.8 Hz), 4.42 (3*H*, m), 4.31 (1*H*, m), 3.80 (3*H*, s); ^{13}C NMR [75 MHz, $(CD_3)_2CO$] δ (major epimer) 161.4, 135.6, 130.8, 129.0, 120.7, 114.3, 103.1, 77.9, 77.1, 69.6, 67.6, 55.5; δ (minor epimer) 161.5, 133.7, 130.3, 129.3, 122.2, 114.3, 104.7, 79.0, 77.9, 70.0, 68.0, 55.5; ν_{max} (NaCl)/cm^{-1} 3518, 3392, 2954, 2907, 2834, 1615, 1515, 1390, 1304, 1248, 1170, 1074, 1050, 1030, 924; MS (EI, 70 eV) 343 and 341 [$(M - H^\cdot)^+$, both 5%], 172 (10), 153 (13), 135 (100), 108 (39), 77 (22), 65 (18), 39 (18).

Refinement

The alcohol hydrogen atoms were included at locations revealed in a difference electron density map and were then refined positionally. Other hydrogen atoms were added at calculated positions (C—H distance 1.0 Å, $U_{iso}(H) = 1.2 \times U_{eq}(C)$) and, during refinement, each was set to ride on the carbon atom to which it is attached.

Figures

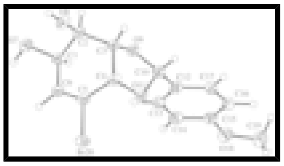


Fig. 1. Anisotropic displacement ellipsoid plot of the major isomer of $C_{14}H_{15}BrO_5$ with labelling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

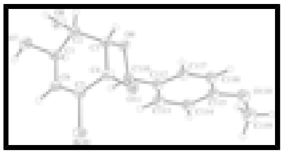


Fig. 2. Anisotropic displacement ellipsoid plot of the minor isomer of $C_{14}H_{15}BrO_5$ with labelling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

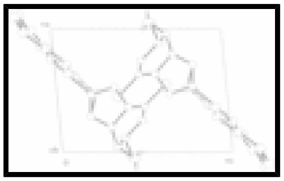


Fig. 3. Unit cell packing diagram of $C_{14}H_{15}BrO_5$ projected down the *b* axis. Hydrogen atoms of the alcohol groups are drawn as circles with small radii and the others have been deleted.

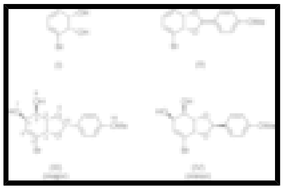


Fig. 4. The structure of (I)–(IV).

Cocrystal of (2*S*,3a*S*,4*R*,5*R*,7a*S*)- and (2*R*,3a*S*,4*R*,5*R*,7a*S*)-7-bromo- 2-(4-methoxyphenyl)-3a,4,5,7a-tetrahydro-1,3-benzodioxole-4,5-diol (17:3)

Crystal data

$C_{14}H_{15}BrO_5$	$F_{000} = 348$
$M_r = 343.17$	$D_x = 1.643$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 30770 reflections
$a = 7.2245$ (4) Å	$\theta = 2.6–27.5°$
$b = 9.7093$ (5) Å	$\mu = 2.98$ mm^{-1}
$c = 9.9373$ (5) Å	$T = 200$ K
$\beta = 95.689$ (3)°	Block, colourless
$V = 693.62$ (6) Å^3	0.40 × 0.29 × 0.26 mm
$Z = 2$	

Data collection

Nonius KappaCCD area-detector diffractometer	2802 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.048$
$T = 200$ K	$\theta_{max} = 27.5°$
φ and ω scans with CCD	$\theta_{min} = 3.5°$
Absorption correction: integration via Gaussian method (Coppens, 1970) implemented in maXus (Mackay *et al.*, 1999)	$h = -9\rightarrow9$
$T_{min} = 0.372$, $T_{max} = 0.586$	$k = -12\rightarrow11$
12613 measured reflections	$l = -12\rightarrow12$
3108 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.030$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.038P)^2 + 0.097P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{max} = 0.043$
$S = 0.99$	$\Delta\rho_{max} = 0.45$ e Å^{-3}

3108 reflections	$\Delta\rho_{\min} = -0.90$ e Å^{-3}
216 parameters	Extinction correction: none
35 restraints	Absolute structure: Flack (1983), with 1430 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.019 (10)

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Br20	0.43964 (4)	0.3005 (3)	0.34759 (3)	0.0547	
O7	1.0479 (3)	0.0958 (4)	0.5926 (3)	0.0594	
O8	1.0545 (3)	0.3760 (4)	0.5778 (2)	0.0476	
O9	0.7101 (3)	0.3574 (4)	0.8155 (2)	0.0468	
O11	0.4712 (3)	0.4076 (4)	0.65992 (19)	0.0444	
O18	0.0214 (4)	0.1796 (4)	1.1172 (3)	0.0562	0.853 (4)
O118	0.0317 (17)	0.3946 (16)	1.1645 (12)	0.0555*	0.147 (4)
C1	0.8881 (4)	0.1684 (4)	0.6274 (3)	0.0414	
C2	0.9556 (3)	0.3090 (5)	0.6760 (2)	0.0382	
C3	0.7968 (4)	0.4054 (4)	0.7008 (3)	0.0406	
C4	0.6353 (4)	0.4100 (4)	0.5872 (3)	0.0367	
C5	0.6293 (3)	0.2884 (5)	0.4953 (2)	0.0374	
C6	0.7390 (4)	0.1786 (4)	0.5112 (3)	0.0397	
C10	0.5344 (5)	0.4276 (5)	0.7997 (3)	0.0398	0.853 (4)
C12	0.4022 (5)	0.3619 (5)	0.8875 (4)	0.0373	0.853 (4)
C13	0.3774 (6)	0.2201 (5)	0.8878 (4)	0.0411	0.853 (4)
C14	0.2495 (6)	0.1620 (5)	0.9669 (5)	0.0473	0.853 (4)
C15	0.1463 (6)	0.2471 (6)	1.0447 (4)	0.0408	0.853 (4)
C16	0.1678 (6)	0.3889 (6)	1.0432 (4)	0.0428	0.853 (4)
C17	0.2976 (6)	0.4437 (6)	0.9649 (4)	0.0411	0.853 (4)
C19	−0.1055 (9)	0.2620 (8)	1.1849 (5)	0.0683	0.853 (4)
C110	0.5244 (13)	0.3003 (17)	0.7692 (10)	0.0396*	0.147 (4)
C112	0.3909 (16)	0.3102 (19)	0.8776 (12)	0.0380*	0.147 (4)
C113	0.294 (2)	0.1981 (19)	0.9244 (16)	0.0469*	0.147 (4)
C114	0.170 (2)	0.219 (2)	1.0228 (16)	0.0414*	0.147 (4)
C115	0.1473 (18)	0.3534 (17)	1.0695 (13)	0.0433*	0.147 (4)
C116	0.246 (2)	0.4612 (17)	1.0201 (15)	0.0403*	0.147 (4)
C117	0.3638 (19)	0.4373 (19)	0.9260 (15)	0.0403*	0.147 (4)
C119	−0.089 (6)	0.292 (4)	1.213 (4)	0.0688*	0.147 (4)
H1	1.006 (7)	0.035 (5)	0.542 (4)	0.0710*	
H2	1.135 (6)	0.342 (4)	0.579 (4)	0.0570*	
H11	0.8363	0.1192	0.7038	0.0491*	
H21	1.0394	0.2984	0.7617	0.0455*	
H31	0.8463	0.5005	0.7188	0.0484*	
H41	0.6399	0.4972	0.5341	0.0439*	
H61	0.7221	0.1014	0.4445	0.0471*	
H101	0.5503	0.5278	0.8211	0.0473*	0.853
H131	0.4513	0.1600	0.8314	0.0489*	0.853
H141	0.2315	0.0599	0.9680	0.0562*	0.853

H161	0.0915	0.4498	1.0971	0.0512*	0.853
H171	0.3164	0.5458	0.9643	0.0492*	0.853
H191	−0.1880	0.2006	1.2334	0.0835*	0.853
H192	−0.0340	0.3240	1.2515	0.0835*	0.853
H193	−0.1832	0.3188	1.1169	0.0835*	0.853
H1101	0.5314	0.2051	0.7316	0.0475*	0.147
H1131	0.312	0.1036	0.8881	0.0563*	0.147
H1141	0.099	0.141	1.0585	0.0497*	0.147
H1161	0.229	0.5569	1.0541	0.0484*	0.147
H1171	0.4335	0.5165	0.8911	0.0484*	0.147
H1191	−0.165	0.335	1.281	0.0826*	0.147
H1192	−0.012	0.215	1.256	0.0826*	0.147
H1193	−0.173	0.255	1.135	0.0826*	0.147

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br20	0.04465 (15)	0.06961 (18)	0.04579 (15)	0.00756 (18)	−0.01518 (10)	−0.00620 (18)
O7	0.0408 (12)	0.0565 (13)	0.0777 (17)	0.0121 (10)	−0.0104 (11)	−0.0169 (12)
O8	0.0301 (10)	0.0530 (13)	0.0602 (14)	0.0004 (9)	0.0068 (10)	0.0097 (10)
O9	0.0317 (9)	0.0736 (13)	0.0343 (9)	0.0055 (8)	−0.0015 (8)	−0.0005 (8)
O11	0.0299 (9)	0.0683 (13)	0.0347 (10)	0.0063 (9)	0.0009 (7)	0.0002 (9)
O18	0.0533 (15)	0.0628 (17)	0.0538 (16)	−0.0029 (13)	0.0123 (13)	0.0109 (13)
C1	0.0332 (13)	0.0424 (14)	0.0471 (16)	0.0012 (11)	−0.0029 (12)	0.0044 (11)
C2	0.0278 (10)	0.0473 (13)	0.0386 (11)	−0.0018 (15)	−0.0018 (8)	0.0010 (16)
C3	0.0319 (13)	0.0486 (14)	0.0404 (14)	0.0008 (11)	−0.0013 (11)	−0.0020 (12)
C4	0.0302 (12)	0.0443 (13)	0.0354 (13)	0.0025 (10)	0.0014 (10)	0.0007 (11)
C5	0.0306 (10)	0.0466 (15)	0.0341 (10)	−0.0029 (13)	−0.0010 (8)	−0.0003 (14)
C6	0.0348 (13)	0.0428 (14)	0.0401 (14)	−0.0020 (11)	−0.0021 (11)	−0.0018 (11)
C10	0.0344 (16)	0.0482 (18)	0.0357 (16)	0.0023 (13)	−0.0025 (13)	−0.0012 (13)
C12	0.0325 (17)	0.045 (2)	0.0333 (17)	0.0037 (15)	−0.0030 (14)	0.0001 (16)
C13	0.036 (2)	0.044 (2)	0.042 (2)	0.0050 (16)	−0.0012 (17)	−0.0032 (16)
C14	0.043 (2)	0.049 (2)	0.048 (2)	0.0008 (17)	−0.0018 (17)	0.0051 (17)
C15	0.0352 (17)	0.053 (3)	0.0336 (18)	−0.0010 (15)	−0.0010 (14)	0.0048 (15)
C16	0.042 (2)	0.049 (2)	0.0373 (19)	−0.0002 (17)	0.0013 (15)	−0.0054 (15)
C17	0.039 (2)	0.045 (2)	0.038 (2)	0.0009 (14)	0.0008 (16)	−0.0036 (15)
C19	0.066 (3)	0.086 (4)	0.057 (3)	−0.011 (2)	0.027 (3)	−0.005 (2)

Geometric parameters (Å, °)

Br20—C5	1.910 (2)	C12—C13	1.388 (5)
O7—C1	1.424 (3)	C12—C17	1.382 (6)
O7—H1	0.82 (5)	C13—C14	1.391 (6)
O8—C2	1.422 (4)	C13—H131	1.000
O8—H2	0.67 (4)	C14—C15	1.397 (6)
O9—C3	1.432 (4)	C14—H141	1.000
O9—C10	1.436 (4)	C15—C16	1.385 (6)
O9—C110	1.482 (11)	C16—C17	1.384 (7)
O11—C4	1.449 (3)	C16—H161	1.000

O11—C10	1.432 (4)	C17—H171	1.000
O11—C110	1.527 (12)	C19—H191	1.000
O18—C15	1.376 (5)	C19—H192	1.000
O18—C19	1.433 (7)	C19—H193	1.000
O118—C115	1.380 (16)	C110—C112	1.518 (15)
O118—C119	1.434 (19)	C110—H1101	1.000
C1—C2	1.512 (5)	C112—C113	1.399 (17)
C1—C6	1.503 (4)	C112—C117	1.346 (17)
C1—H11	1.000	C113—C114	1.406 (17)
C2—C3	1.520 (4)	C113—H1131	1.000
C2—H21	1.000	C114—C115	1.397 (17)
C3—C4	1.542 (4)	C114—H1141	1.000
C3—H31	1.000	C115—C116	1.382 (16)
C4—C5	1.490 (4)	C116—C117	1.347 (16)
C4—H41	1.000	C116—H1161	1.000
C5—C6	1.328 (4)	C117—H1171	1.000
C6—H61	1.000	C119—H1191	1.000
C10—C12	1.498 (6)	C119—H1192	1.000
C10—H101	1.000	C119—H1193	1.000

C1—O7—H1	104 (4)	C14—C13—H131	120.1
C2—O8—H2	105 (3)	C13—C14—C15	119.6 (4)
C3—O9—C10	102.1 (2)	C13—C14—H141	120.2
C3—O9—C110	109.2 (4)	C15—C14—H141	120.2
C4—O11—C10	106.5 (2)	C14—C15—O18	115.0 (4)
C4—O11—C110	101.9 (5)	C14—C15—C16	121.0 (5)
C15—O18—C19	117.6 (3)	O18—C15—C16	124.0 (4)
C115—O118—C119	117.1 (16)	C15—C16—C17	118.1 (5)
O7—C1—C2	106.3 (2)	C15—C16—H161	120.9
O7—C1—C6	112.5 (2)	C17—C16—H161	120.9
C2—C1—C6	111.7 (2)	C16—C17—C12	122.0 (4)
O7—C1—H11	108.8	C16—C17—H171	119.0
C2—C1—H11	108.8	C12—C17—H171	119.0
C6—C1—H11	108.8	O18—C19—H191	109.5
C1—C2—O8	111.3 (2)	O18—C19—H192	109.5
C1—C2—C3	112.5 (2)	H191—C19—H192	109.5
O8—C2—C3	105.5 (3)	O18—C19—H193	109.5
C1—C2—H21	109.1	H191—C19—H193	109.5
O8—C2—H21	109.1	H192—C19—H193	109.5
C3—C2—H21	109.1	O11—C110—O9	97.0 (8)
C2—C3—O9	109.0 (2)	O11—C110—C112	109.2 (8)
C2—C3—C4	115.3 (2)	O9—C110—C112	112.0 (8)
O9—C3—C4	103.5 (2)	O11—C110—H1101	112.5
C2—C3—H31	109.6	O9—C110—H1101	112.6
O9—C3—H31	109.6	C112—C110—H1101	112.5
C4—C3—H31	109.6	C110—C112—C113	124.2 (12)
C3—C4—O11	103.4 (2)	C110—C112—C117	115.9 (12)
C3—C4—C5	113.5 (2)	C113—C112—C117	119.9 (11)
O11—C4—C5	108.5 (2)	C112—C113—C114	119.5 (12)
C3—C4—H41	110.4	C112—C113—H1131	120.2

O11—C4—H41	110.4	C114—C113—H1131	120.3
C5—C4—H41	110.4	C113—C114—C115	118.1 (13)
Br20—C5—C4	113.4 (2)	C113—C114—H1141	121.0
Br20—C5—C6	121.0 (2)	C115—C114—H1141	121.0
C4—C5—C6	125.6 (2)	C114—C115—O118	126.5 (12)
C1—C6—C5	121.2 (2)	C114—C115—C116	120.5 (11)
C1—C6—H61	119.4	O118—C115—C116	113.0 (11)
C5—C6—H61	119.4	C115—C116—C117	120.0 (12)
O9—C10—O11	103.6 (2)	C115—C116—H1161	120.0
O9—C10—C12	109.9 (3)	C117—C116—H1161	120.0
O11—C10—C12	110.3 (3)	C116—C117—C112	122.0 (12)
O9—C10—H101	110.9	C116—C117—H1171	119.0
O11—C10—H101	110.9	C112—C117—H1171	119.0
C12—C10—H101	110.9	O118—C119—H1191	109.4
C10—C12—C13	120.9 (4)	O118—C119—H1192	109.5
C10—C12—C17	119.6 (4)	O118—C119—H1193	109.5
C13—C12—C17	119.4 (5)	H1191—C119—H1192	109.5
C12—C13—C14	119.8 (5)	H1191—C119—H1193	109.5
C12—C13—H131	120.1	H1192—C119—H1193	109.5

C10—O9—C3—C2	−162.1 (3)	C2—C3—C4—C5	19.4 (4)
C10—O9—C3—C4	−38.9 (4)	O9—C3—C4—O11	17.8 (4)
C3—O9—C10—O11	46.4 (4)	O11—C4—C5—Br20	69.7 (3)
C3—O9—C10—C12	164.3 (3)	O11—C4—C5—C6	−109.0 (3)
C10—O11—C4—C3	10.3 (4)	C3—C4—C5—C6	5.3 (4)
C10—O11—C4—C5	131.2 (3)	C3—C4—C5—Br20	−175.9 (2)
C4—O11—C10—O9	−35.0 (4)	Br20—C5—C6—C1	−179.8 (2)
C4—O11—C10—C12	−152.7 (4)	C4—C5—C6—C1	−1.2 (5)
C19—O18—C15—C14	−172.0 (4)	O9—C10—C12—C13	−48.6 (5)
C19—O18—C15—C16	6.0 (6)	O9—C10—C12—C17	134.2 (4)
O7—C1—C2—C3	173.0 (2)	O11—C10—C12—C13	65.1 (5)
C6—C1—C2—O8	−68.3 (3)	O11—C10—C12—C17	−112.1 (4)
O7—C1—C2—O8	54.8 (3)	C10—C12—C13—C14	−177.9 (4)
C2—C1—C6—C5	−27.0 (4)	C17—C12—C13—C14	−0.7 (6)
C6—C1—C2—C3	49.9 (3)	C13—C12—C17—C16	−0.1 (6)
O7—C1—C6—C5	−146.4 (3)	C10—C12—C17—C16	177.2 (4)
C1—C2—C3—C4	−47.1 (4)	C12—C13—C14—C15	0.4 (6)
O8—C2—C3—O9	−169.8 (2)	C13—C14—C15—O18	178.9 (4)
O8—C2—C3—C4	74.3 (3)	C13—C14—C15—C16	0.7 (7)
C1—C2—C3—O9	68.7 (3)	C14—C15—C16—C17	−1.5 (6)
O9—C3—C4—C5	−99.6 (3)	O18—C15—C16—C17	−179.4 (4)
C2—C3—C4—O11	136.7 (3)	C15—C16—C17—C12	1.2 (6)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H1···O8^{i}	0.81 (4)	1.97 (5)	2.779 (5)	171 (5)
O8—H2···O7	0.67 (4)	2.48 (4)	2.725 (5)	105 (4)
O8—H2···O11^{ii}	0.67 (4)	2.56 (4)	3.055 (3)	133 (4)

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+1; (ii) *x*+1, *y*, *z*.

Fig. 1

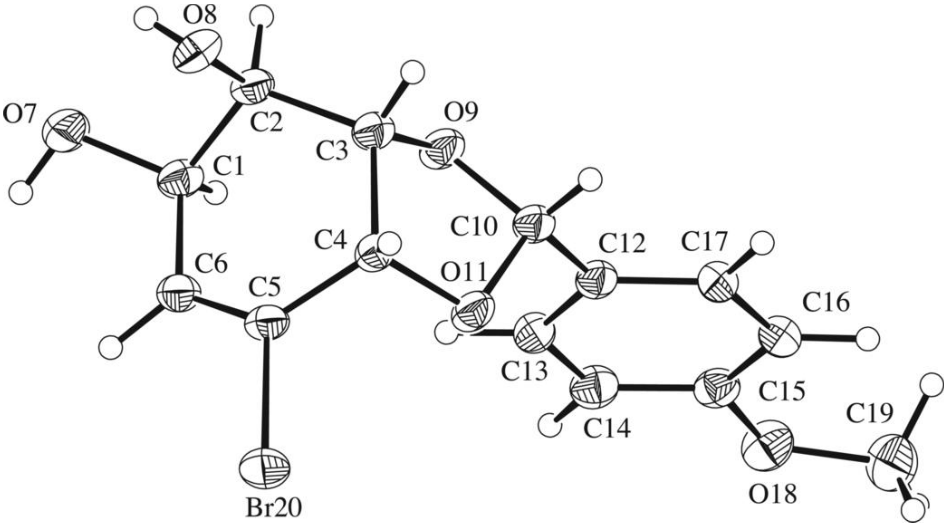


Fig. 2

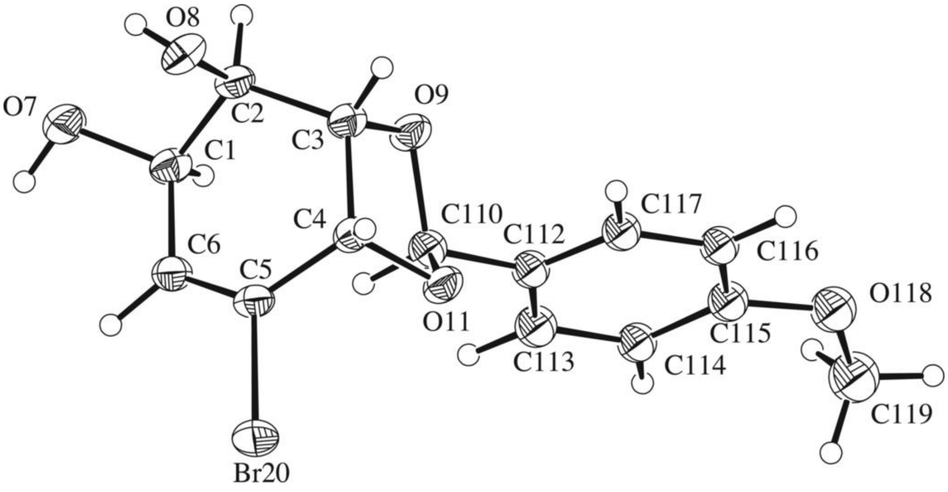

O8
O7
C2
C1
C3
O9
C4
C110
C112
C117
C116
C6
C5
O11
O118
C115
C113
C114
C119
Br20

Fig. 3

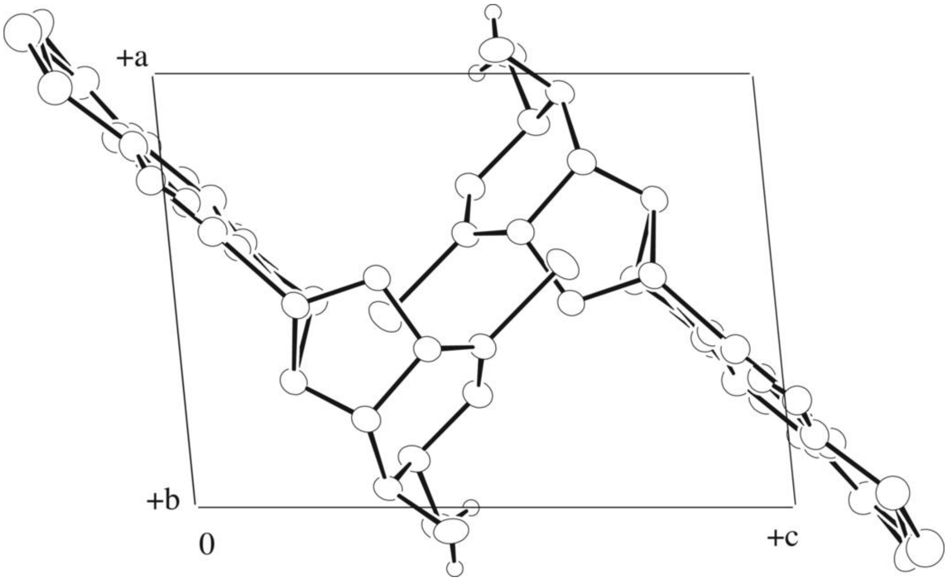
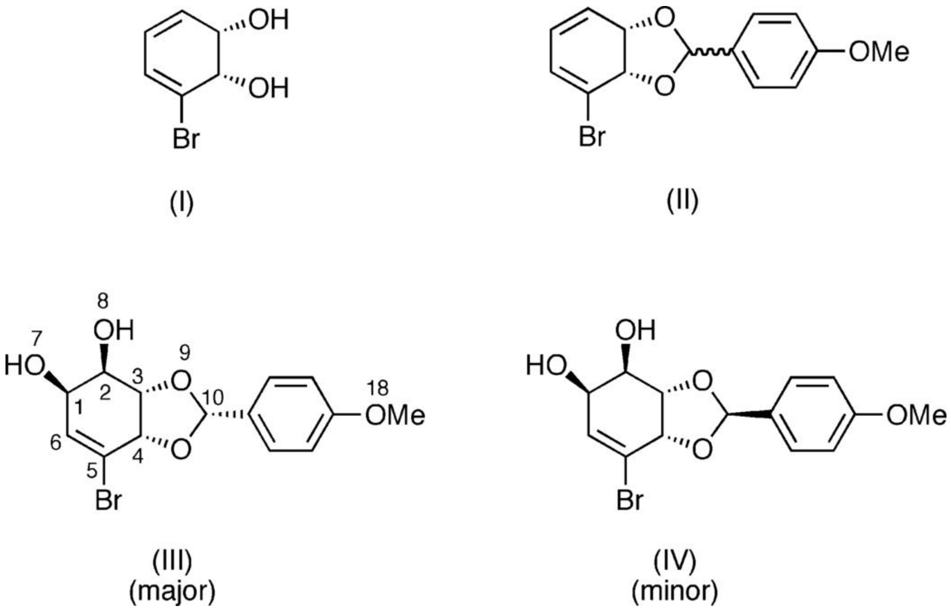


Fig. 4


OH
OH
Br
(I)
O
O
OMe
Br
(II)
8
OH
7
HO
9
2
3
1
O
10
18
OMe
6
O
4
5
Br
(III)
(major)
OH
HO
O
OMe
O
Br
(IV)
(minor)