

Marchantin M trimethyl ether

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The title macrocycle, C₃₁H₃₀O₅, is comprised of two bibenzyl ether moieties linked cyclically by spacers which each consist of two-carbon alkyl chains. The observed conformation of the macrocycle may be partly stabilized by intramolecular C—H···O close contacts. The packing appears to be directed by van der Waals forces. This work explains the occurrence of a signal found in the ¹H NMR spectra of both marchantinquinone and marchantin M trimethyl ether at δ = 5.49 and 5.56 p.p.m., respectively. The shift in the position of the expected peak can be explained by the proximity of an H atom belonging to one of the aromatic rings to another ring in the same molecule.

Comment

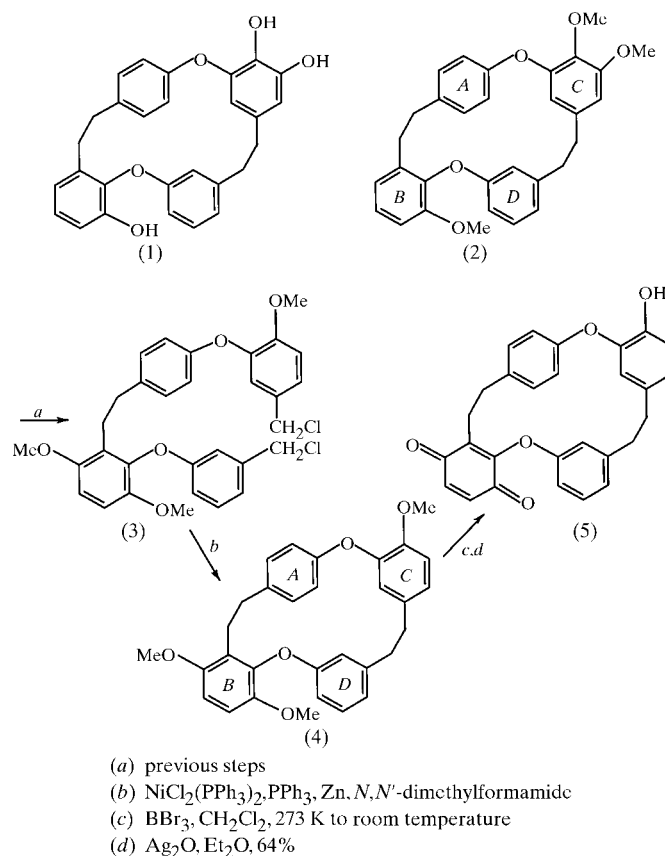
Bryophytes constitute a notable reserve of structurally new natural products (Zinsmeister *et al.*, 1991). Recently, many of their secondary metabolites have been shown to display a wide range of biological activities (Asakawa, 1995). This fact, together with the exclusive occurrence of some natural products in these plants, has produced a renewed interest in bryophyte chemistry. In particular, numerous cyclic and acyclic bis(bibenzyl) systems, such as perrottetins, marchantins and riccardins, are found only in these plants (Asakawa, 1982).

The structural analysis of these systems is generally performed through intermediate precursors because of difficulties in obtaining crystals suitable for X-ray diffraction analysis. For instance, the crystal structure of marchantin A trimethyl ether, (2) (Taira *et al.*, 1994), was determined because marchantin A itself, (1), was not available as single crystals.

A quinone of this type, named marchantinquinone, was isolated from extracts of *Reboulia hemisphaerica*, formerly described as *Mannia subpilosa*, and studied by ¹H and ¹³C NMR spectroscopy (Wei & Wu, 1991). This compound, possessing a *p*-quinone structure embedded in an 18-

membered macrocycle, was the first bis(bibenzyl) diether with a quinone structure isolated from bryophytes. In addition to its novel structure, marchantinquinone has interesting biological activity (Wei *et al.*, 1995). Although this compound has been recently synthesized (López *et al.*, 2000), until now, no crystal-structure determination has been reported because of the difficulty in obtaining suitable single crystals.

The final step of the synthesis of marchantinquinone, (5) (López *et al.*, 2000), involves the macrocyclization from a dichloride precursor, (3), using an active [Ni]⁰ complex under high dilution conditions, giving marchantin M trimethyl ether, (4), as an intermediate product. This report presents the structure determination of this intermediate product and provides information of interest which may be related to the expected orientations of the aromatic rings in the final quinone product.



The structure of the title compound consists of monomeric units of a macrocyclic bis(bibenzyl) ether (Fig. 1). For simplicity, the four aromatic rings will be called A, B, C and D, corresponding to C9–C14, C1–C6, C15–C20 and C23–C28, respectively. The bibenzyl ether units are linked by two-carbon chains: C7–C8 relating A and B, and C21–C22 relating C and D. The dihedral angles between the planes of the rings are A/B = 49.13 (8), A/C = 84.52 (8), A/D = 43.5 (1), B/C = 78.94 (9), B/D = 65.9 (1) and C/D = 42.38 (9)°. The equivalent dihedral angles in marchantin A trimethyl ether (Taira *et al.*, 1994) are A/B = 50.64, A/C = 82.43, A/D = 46.18, B/C = 70.45, B/D = 67.61 and C/D = 52.75°. The ring centroid-centroid distances of the title compound are A/B = 5.47, A/C =

4.80, $A/D = 4.42$, $B/C = 8.72$, $B/D = 4.85$ and $C/D = 4.51$ Å, while the equivalent distances in marchantin A trimethyl ether (Taira *et al.*, 1994) are $A/B = 4.79$, $A/C = 4.76$, $A/D = 4.55$, $B/C = 8.80$, $B/D = 4.79$ and $C/D = 4.74$ Å. As can be seen from these values, the conformation is very similar for both compounds. Table 2 includes some important torsion angles of molecules (1) and (4) showing that the conformations of molecules (1) and (4) are very similar. A minor difference is the rotation of the *A* ring around the C9→C12 axis, as can be seen from a comparison of the following torsion angles: C7—C8—C9—C10, C7—C8—C9—C14, C13—C12—O2—C15 and C11—C12—O2—C15. The other slight difference is found in ring *C*, mainly in the C21—C22—C23—C28 and C21—C22—C23—C24 torsion angles. The similar conformations of both molecules indicate that the presence of different substituents in the *B* and *C* rings does not considerably affect their overall shapes and suggests that marchantinquinone (5) could exhibit a similar conformation.

The structure includes two intramolecular C—H···O close contacts which may partly stabilize the observed conformation of the macrocycle, *i.e.* C7—H7B···O1 and C8—H8B···O4. Geometric parameters which characterize these interactions are 0.97 and 0.97 Å, 2.40 and 2.56 Å, 2.857 (4) and 3.080 (3) Å, and 108 and 114° for C—H, H···O, C···O and C—H···O, respectively. The absence of intermolecular hydrogen bonds and π contacts suggests that the crystal packing is directed by van der Waals forces.

An apparent anomaly observed in the ^1H NMR spectra of both marchantinquinone and marchantin M trimethyl ether (Wei & Wu, 1991; López *et al.*, 2000) can be interpreted from the present structural study. The signal found at $\delta = 5.49$ p.p.m. (5.56 p.p.m. for marchantinquinone) for H20 can now be explained by the proximity of H20 and the aromatic *D* ring which shifts the peak to higher fields. The perpendicular distance from H20 to the plane of the ring is 3.01 Å and the distances to the centre of the ring from H20 and C20 are 3.30 and 3.67 Å, respectively.

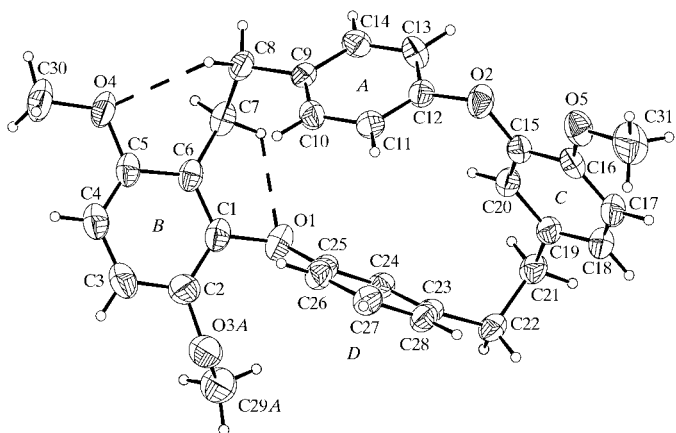


Figure 1

View of the title compound with displacement ellipsoids drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii. Short C—H···O contacts are represented by dashed lines. Only one of the two disordered positions for the O3—C29 residue is shown to improve clarity.

Experimental

The synthesis of the title compound has been reported fully in a previous article (López *et al.*, 2000). Colourless crystals suitable for diffraction analysis were obtained by vapour diffusion of hexane into a solution of the title compound in chloroform.

Crystal data

$\text{C}_{31}\text{H}_{30}\text{O}_5$	$D_x = 1.277$ Mg m $^{-3}$
$M_r = 482.52$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 22 reflections
$a = 14.937$ (3) Å	$\theta = 20.15$ – 23.25°
$b = 9.316$ (5) Å	$\mu = 0.086$ mm $^{-1}$
$c = 18.262$ (2) Å	$T = 293$ (2) K
$\beta = 98.877$ (12) $^\circ$	Prism, colourless
$V = 2510.7$ (15) Å 3	$0.31 \times 0.24 \times 0.08$ mm
$Z = 4$	

Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.089$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 27.47^\circ$
Absorption correction: ψ scan	$h = -2 \rightarrow 19$
(Molecular Structure Corporation, 1993)	$k = 0 \rightarrow 12$
$T_{\text{min}} = 0.975$, $T_{\text{max}} = 0.993$	$l = -23 \rightarrow 23$
6844 measured reflections	3 standard reflections
5746 independent reflections	every 150 reflections
2380 reflections with $I > 2\sigma(I)$	intensity decay: 4.3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$\Delta\rho_{\text{max}} = 0.18$ e Å $^{-3}$
$wR(F^2) = 0.193$	$\Delta\rho_{\text{min}} = -0.20$ e Å $^{-3}$
$S = 0.983$	Extinction correction: SHELXL97
5746 reflections	(Sheldrick, 1997)
345 parameters	Extinction coefficient: 0.016 (2)
All H atoms were constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

One of the methoxy groups in ring *B* is disordered. The occupancies of two positions were refined and converged to 0.514 (7) for the residue O3A, C29A and H29A,B,C. The occupancy of the other residue was constrained so that both add to unity. The H atoms were placed at geometrically suitable positions and refined riding with fixed isotropic displacement parameters $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atom, except for those belonging to C29, C30 and C31 where the isotropic displacement parameters were fixed at $U_{\text{iso}} = 1.5U_{\text{eq}}$ of the parent atom.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1993); cell refinement: MSC/AFC Diffractometer Control Software; data reduction: MSC/AFC Diffractometer Control Software; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure:

Table 1

Selected geometric parameters (Å, $^\circ$).

O1—C25	1.389 (3)	O2—C15	1.386 (3)
O1—C1	1.403 (3)	C16—O5	1.376 (3)
C2—O3A	1.414 (5)	O3A—C29A	1.416 (6)
C2—O3B	1.419 (5)	O3B—C29B	1.428 (6)
C5—O4	1.374 (3)	O4—C30	1.425 (3)
C12—O2	1.402 (3)	O5—C31	1.414 (3)
C25—O1—C1	118.4 (2)	C2—O3B—C29B	111.6 (6)
C15—O2—C12	117.02 (18)	C5—O4—C30	117.6 (3)
C2—O3A—C29A	108.1 (6)	C16—O5—C31	117.0 (3)

Table 2

Comparison of the conformations of marchantin M trimethyl ether, (4), and marchantin A trimethyl ether, (1) (torsion angles, °).

	(4)	(1)
C25—O1—C1—C6	125.1 (3)	116.7 (4)
C25—O1—C1—C2	-61.6 (3)	-65.8 (5)
C1—C6—C7—C8	-111.7 (3)	-119.2 (4)
C5—C6—C7—C8	72.2 (3)	68.1 (5)
C6—C7—C8—C9	85.1 (3)	90.5 (6)
C7—C8—C9—C10	-79.5 (3)	-71.3 (7)
C7—C8—C9—C14	99.4 (3)	104.1 (6)
C13—C12—O2—C15	-91.4 (3)	-104.8 (5)
C11—C12—O2—C15	92.5 (3)	76.5 (5)
C12—O2—C15—C20	9.9 (4)	14.3 (6)
C12—O2—C15—C16	-169.4 (2)	-167.6 (4)
C18—C19—C21—C22	89.0 (3)	88.8 (5)
C20—C19—C21—C22	-87.0 (3)	-89.7 (5)
C19—C21—C22—C23	57.0 (3)	62.0 (5)
C21—C22—C23—C28	-99.2 (3)	-111.0 (5)
C21—C22—C23—C24	77.9 (3)	70.5 (5)
C1—O1—C25—C26	-13.5 (4)	-7.2 (5)
C1—O1—C25—C24	167.7 (2)	172.9 (3)

SHELXL97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1103). Services for accessing these data are described at the back of the journal.

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