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Key indicators

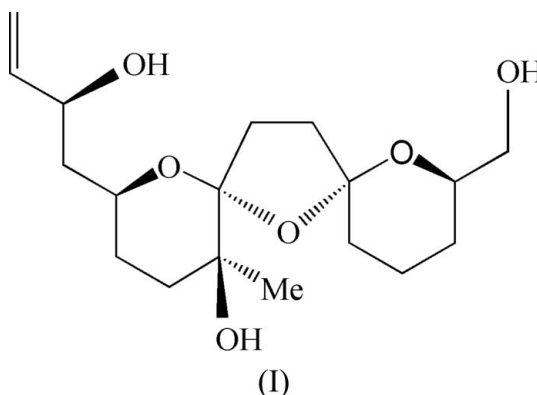
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.040
 wR factor = 0.041
Data-to-parameter ratio = 7.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(3*S*,2'*S*,5'*S*,6'*R*,8'*R*,10'*R*)-3-Hydroxy-4-(5'-hydroxy-10'-hydroxymethyl-5'-methyl-1',7',9'-trioxadispiro[5.1.5.2]pentadec-2'-yl)but-1-ene**

The configurations of four of the six chiral centers in the title compound, $\text{C}_{18}\text{H}_{30}\text{O}_6$, are the same as those in pinnatoxin A, while one is inverted. The configuration of the sixth chiral center, which has no equivalent in pinnatoxin A, has also been determined. The overall molecular structure is stabilized by intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

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Comment

In the study of stereoselective syntheses of the *BCD* ring system of pinnatoxin A (Noda *et al.*, 1998; Sakamoto *et al.*, 2004), the title compound, (I), was obtained. The structure of (I) (Fig. 1) is reported here. The configurations of C14(*S*), C9(*R*), C6(*R*) and C2(*R*) are the same as those in pinnatoxin A, but that of C10(*S*) is inverted. The configuration of the sixth chiral center in (I), which has no equivalent in pinnatoxin A, has been determined as C16(*S*). There are no unusual bond distances nor bond angles in (I). The C—O bond distances are in the range 1.414 (3)–1.452 (3) Å, and the $\text{Csp}^3-\text{Csp}^3$ distances are in the range 1.511 (4)–1.540 (4) Å. The bond angles about the Csp^3 atoms are not much different from the tetrahedral angle of 109.5° , the largest deviation being for C7—C8—C9 [102.6 (2)°].



The molecular structure is stabilized by several intramolecular hydrogen bonds (Table 1). In particular, O1—H1 \cdots O6 binds the head and tail of the molecule. Atom O1 also accepts an intermolecular hydrogen bond from the hydroxy group O5—H18.

Experimental

Compound (I) was synthesized by the procedure described by Sakamoto *et al.* (2004). Recrystallization from an ethyl acetate–diethyl ether (1:1) solution at room temperature gave colourless block-shaped crystals of (I).

Crystal data

$C_{18}H_{30}O_6$
 $M_r = 342.42$
 Orthorhombic, $P2_12_12_1$
 $a = 11.822$ (5) Å
 $b = 16.841$ (8) Å
 $c = 9.117$ (5) Å
 $V = 1815.1$ (15) Å³

$Z = 4$
 $D_x = 1.253$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 296.1$ K
 Block, colorless
 $0.55 \times 0.45 \times 0.35$ mm

Data collection

Rigaku AFC-5S diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.941$, $T_{\max} = 0.968$
 2380 measured reflections
 2377 independent reflections

1690 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.004$
 $\theta_{\text{max}} = 27.5^\circ$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.3%

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.041$
 $S = 1.53$
 1690 reflections
 217 parameters

H-atom parameters constrained
 $w = 1/[0.0002F_o^2 + \sigma^2(F_o)]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.15$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots O2$	0.79	2.58	2.869 (3)	104
$O1-H1\cdots O6$	0.79	2.09	2.875 (3)	170
$O6-H27\cdots O4$	0.78	2.11	2.791 (3)	146
$O5-H18\cdots O1^i$	0.71	2.08	2.764 (3)	164

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

The H atoms of the vinyl group and the three hydroxyl groups were located in difference Fourier syntheses. The remaining 24 H atoms were placed in geometrically calculated positions ($C-H = 0.95$ Å). All of them were allowed to ride on their parent atoms with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(\text{parent atom})$. The absolute configuration of (I) has been assigned by reference to the four unchanging chiral centers $C14(S)$, $C9(R)$, $C6(R)$ and $C2(R)$ in the synthetic procedures (Sakamoto *et al.*, 2004). No Friedel pairs were measured.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation and Rigaku, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CrystalStructure*; molecular graphics:

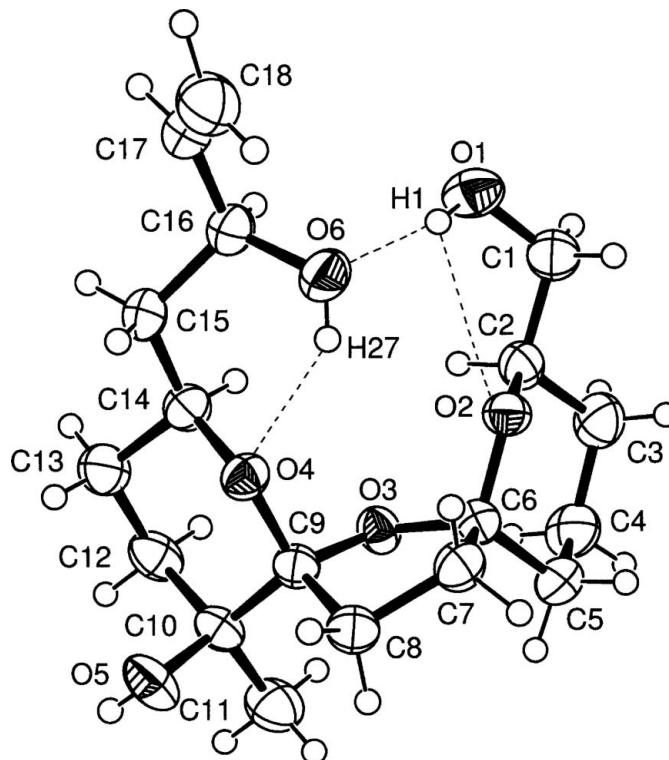


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids. Dashed lines indicate intramolecular hydrogen bonds.

ORTEP (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

References

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