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Revision of the structure of podocarpaside *E*, from *Actaea podocarpa*

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Key indicators

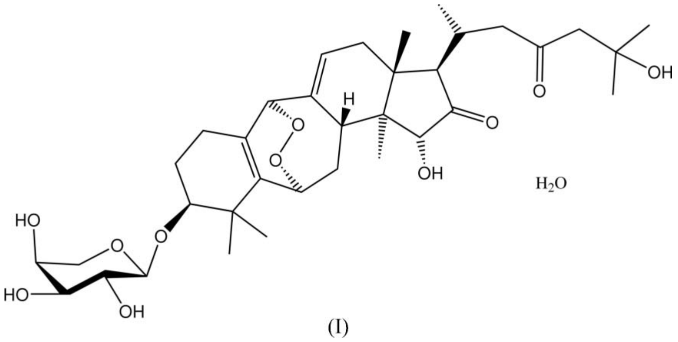
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.081
Data-to-parameter ratio = 8.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, (I), 3β,15α,25-trihydroxy-16,23-dioxo-6α,19α-epidioxy-9,10-*seco*-9,19-cyclolanost-5(10),9(11)-diene 3-*O*-α-L-arabinopyranoside, crystallizes as the monohydrate, $C_{35}H_{52}O_{11}\cdot H_2O$. It has an *endo*-epoxide rather than two OH groups on its seven-membered ring. The O—O distance is 1.473 (3) Å, and the C—O—O—C torsion angle is −30.4 (3)°. O···O distances in hydrogen bonds are in the range 2.679 (3)–3.015 (3) Å.

Comment

We recently described (Ali *et al.*, 2007) the isolation and characterization of podocarpasides *A*–*G*, which are 9,10-*seco*-9,19-cyclolanostane arabinosides from the roots of *Actaea podocarpa*. This species, found in forests of the high Appalachian Mountains of the eastern USA, is closely related to black cohosh, a well known herbal medicine useful for treatment of menstrual pain and menopausal disorders.



(I)

One constituent, podocarpaside *D*, was characterized by crystal structure determination, and the others by spectroscopic methods, including extensive two-dimensional NMR techniques. The title compound was spectroscopically characterized as having β-OH groups at C6 and C19, based partially on a small pseudomolecular ion peak in the HRESIMS spectrum, which suggested the formula $C_{35}H_{54}O_{11}$. Crystals of the monohydrate, (I), have now been grown, and their structure (Fig. 1) reveals an α-*endo*-epoxide bridging the seven-membered ring, rather than two OH groups. Re-recorded HRESIMS on crystalline podocarpaside *E* clearly showed a larger pseudomolecular ion peak, corresponding to the formula found by the crystal structure determination, and we conclude that our previous interpretation of the spectroscopic data (Ali *et al.*, 2007) was incorrect.

Selected geometric paramaters for (I) are given in Table 1. While podocarpaside *D* has an extended conformation, the epoxidation of the seven-membered ring, as well as the β

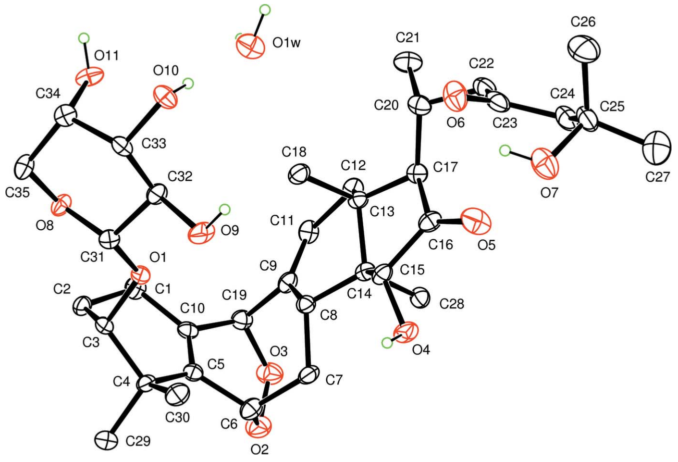


Figure 1

The asymmetric unit of (I), with 50% probability displacement ellipsoids, showing the atom-numbering scheme. H atoms on C are not shown.

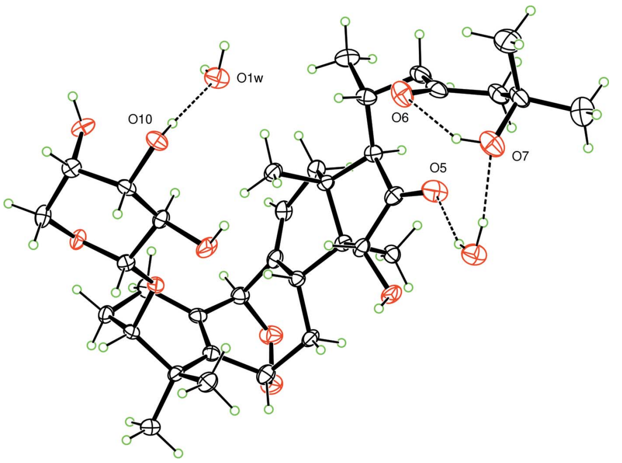


Figure 2

A view showing the intramolecular hydrogen bond and hydrogen bonding to water molecules (dashed lines). H atoms are shown with arbitrary radius, and the unlabelled water molecule is related by the symmetry operator (x + 1, y, z).

orientation of the arabinose substituent, impart a folded conformation to (I). The water molecule is inside the fold, where it is the donor in two hydrogen bonds and the acceptor for a third. There is also an O—H···O intramolecular hydrogen bond (Table 2).

Experimental

The isolation of podocarpaside *E* has been described previously (Ali *et al.*, 2007). Crystals of the monohydrate, (I), were grown from undried methanol.

Crystal data

$C_{35}H_{52}O_{11}\cdot H_2O$
M_r = 666.78
Orthorhombic, $P2_12_12_1$
a = 7.6672 (15) Å
b = 15.324 (3) Å
c = 29.260 (6) Å

V = 3437.8 (12) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100 K
0.42 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer (with Oxford Cryostream cooler)
Absorption correction: none

11976 measured reflections
3870 independent reflections
2917 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.081
S = 1.03
3870 reflections
443 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.21 e $Å^{-3}$
$\Delta\rho_{\rm min}$ = −0.22 e $Å^{-3}$

Table 1

Selected geometric parameters (Å, °).

O2—C6	1.438 (3)	C5—C10	1.330 (4)
O2—O3	1.473 (3)	C9—C11	1.336 (4)
O3—C19	1.447 (4)		
C6—O2—O3	109.6 (2)	C19—O3—O2	113.29 (19)
C6—O2—O3—C19	−30.4 (3)	C7—C8—C9—C19	36.3 (3)
C10—C5—C6—C7	77.4 (3)	C6—C5—C10—C19	−8.7 (4)
C5—C6—C7—C8	−27.5 (4)	C5—C10—C19—C9	−76.9 (3)
C6—C7—C8—C9	−51.3 (3)	C8—C9—C19—C10	51.3 (3)

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O11$^{\rm i}$	0.84	1.99	2.762 (3)	152
O7—H7···O6	0.84	2.22	2.838 (3)	130
O9—H9···O10$^{\rm ii}$	0.84	2.28	3.015 (3)	146
O10—H10···O1W	0.84	1.86	2.683 (3)	165
O11—H11···O10$^{\rm iii}$	0.84	1.86	2.679 (3)	163
O1W—H2W···O5$^{\rm iv}$	0.97 (4)	1.92 (4)	2.815 (3)	153 (3)
O1W—H1W···O7$^{\rm iv}$	0.87 (3)	1.99 (3)	2.847 (3)	171 (3)

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

H atoms on C were placed in idealized positions, with C—H distances of 0.95–1.00 Å, and treated as riding. H atoms of OH groups positioned to give optimum fit to the observed electron density, with O—H = 0.84 Å and C—O—H = 109.5°. A torsional parameter was refined for each methyl and OH group. The coordinates of the water H atoms were refined. $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent), or 1.5$U_{\rm eq}$(parent) for methyl and OH. The absolute configuration could not be determined, but was assigned to correspond with that of α-L-arabinose. Friedel pairs were averaged.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK*; data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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