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(20*S*)-2*α*,3*β*,12*β*-Trihydroxydammar-24-ene 20-*O*-*β*-D-glucopyranoside (Gynosaponin TN1) as the 2.5-methanol solvate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean *σ*(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.055
wR factor = 0.158
Data-to-parameter ratio = 11.3

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

A crystal structure establishing the relative sterochemistry of the title compound, $C_{36}H_{62}O_9{\cdot}2.5CH_3OH$, has been obtained from single-crystal X-ray diffraction data at 150 K. The relative stereochemistry is in accord with previous stereochemistry assignments based on mass spectroscopy and NMR spectroscopy. The asymmetric unit contains two crystallographically independent dammar-24-ene molecules, together with five methanol solvent molecules; one of the solvent molecules is disordered over two sites with occupancies of 0.5. Hydrogen bonds link the two dammar-24-ene molecules and the methanol molecules together into an intricate network, with donor–acceptor distances ranging from 2.646 (8) to 3.227 (3) Å.

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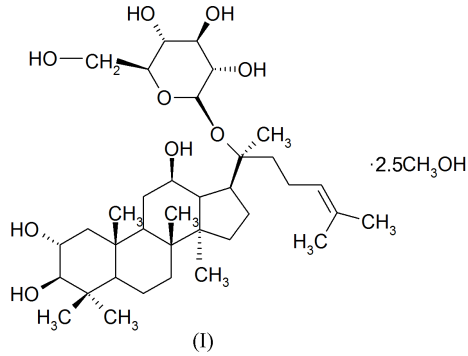
Comment

Gynostemma pentaphyllum (*Thunb.*) Makino belongs to the family Cucurbitaceae. This perennial climbing herb is mainly found in southern tropical areas of Asia. *Gynostemma* saponins, termed gypenosides or gynosaponins, are prominent compounds in the plant and exist mainly as dammarane-type triterpene glycosides (China Pharmaceutical University, 1996). Saponins from *Gynostemma* are similar in structure to ginsenosides, the saponins from *Panax ginseng* (*Araliaceae*). Like ginsenosides, gynosaponins are also believed to be associated with the biological actions of *Gynostemma*, including hypocholesterolaemic, antiulcer, antitumour and antioxidant activities (Cui *et al.*, 1999). Gynosaponin TN1, (I), has been linked with anti-tumour activity (Takemoto *et al.*, 1984). Takemoto *et al.* (1984) and Nagai *et al.* (1981) reported the stereochemistry of TN1 on the basis of mass spectrometry and ^{1}H and ^{13}C NMR results *via* chemical degradation to aglycone and sugar moieties and comparison with compounds of closely related structures. This paper reports the relative stereochemistry of TN1 as determined by X-ray crystallography.



(I)

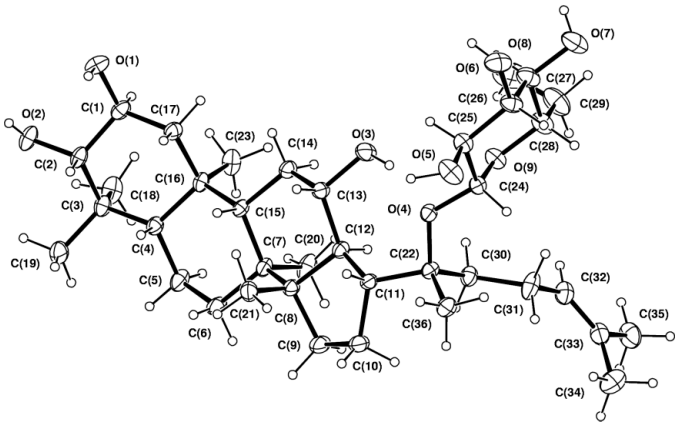


Figure 1
A view of molecule 1 of (I), with displacement ellipsoids shown at the 50% level.

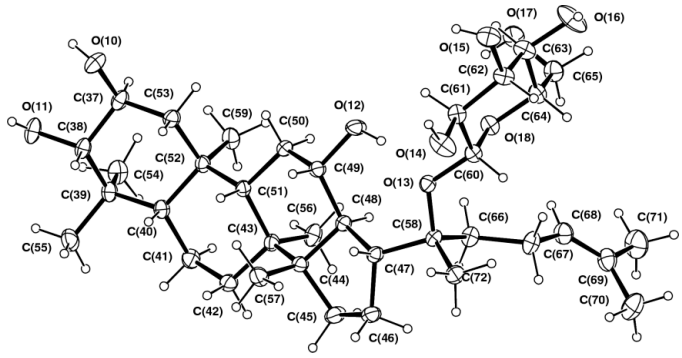


Figure 2
A view of molecule 2 of (I), with displacement ellipsoids shown at the 50% level.

Experimental

Plant material from *Gynostemma pentaphyllum* (*Thunb.*) Makino cultivated in Sydney, Australia, was dried and milled to a fine powder. The material was extracted first with water and then with ethanol. The ethanol extract was concentrated down to a partial solid residue under reduced pressure and then dissolved in a solution of dichloromethane–ethanol (5:1) (a few drops of water and methanol were added for complete dissolution). The mixture was fractionated by short-column normal-phase silica-gel vacuum chromatography with an increasing ethanol gradient and collected at 100 ml intervals. Dried fractions of the dichloromethane–ethanol gradient 2:1 to 1:1 were combined, dissolved in methanol and ethyl acetate, and left at ambient temperature. The resulting white crystals were filtered and dried. ^{1}H and ^{13}C NMR spectra of these crystals were consistent with the published data for TN1 (Takemoto *et al.*, 1984; Nagai *et al.*, 1981). Recrystallization was achieved by dissolving the dried TN1 crystals in methanol with heating. The solution, which was left overnight at room temperature, produced two large prominent single crystals of TN1.

Crystal data

$C_{36}H_{62}O_9\cdot2.5CH_4O$
M_r = 718.96
Orthorhombic, $P2_12_12_1$
a = 10.4015 (16) Å
b = 23.653 (4) Å
c = 32.204 (5) Å
V = 7923 (2) Å^3
Z = 8
D_x = 1.205 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1007 reflections
θ = 2.6–28.1°
μ = 0.09 mm^{-1}
T = 150 (2) K
Prism, colourless
0.46 × 0.43 × 0.38 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: none
78 268 measured reflections
10 572 independent reflections
9296 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 28.3°
$h = -13 \rightarrow 13$
$k = -30 \rightarrow 31$
$l = -41 \rightarrow 42$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.158
S = 1.38
10572 reflections
936 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O7^{i}	0.84	1.99	2.829 (3)	174
O2—H2O···O1	0.84	2.70	2.843 (3)	91
O3—H3O···O4	0.84	1.87	2.680 (3)	163
O3—H3O···O9	0.84	2.58	3.227 (3)	135
O5—H5O···O23B^{ii}	0.98	1.72	2.668 (8)	161
O5—H5O···O23A^{ii}	0.98	1.84	2.753 (7)	154
O6—H6O···O21	0.84	1.96	2.756 (4)	158
O7—H7O···O17	0.84	1.92	2.745 (3)	167
O8—H8O···O19	0.84	1.97	2.693 (4)	143
O10—H10···O1^{ii}	0.84	1.98	2.737 (3)	150
O11—H11O···O15^{i}	0.84	2.10	2.857 (3)	150
O12—H12O···O13	0.84	1.82	2.648 (3)	167
O14—H14O···O5^{iii}	0.84	2.07	2.712 (3)	133
O15—H15O···O8	0.84	2.46	2.790 (4)	104
O16—H16O···O10^{iv}	0.84	1.88	2.688 (3)	160
O17—H17O···O21	0.84	1.98	2.776 (3)	157
O19—H19O···O3	0.84	1.91	2.676 (4)	150
O20—H20O···O14	0.84	1.99	2.770 (4)	153
O21—H21O···O12	0.84	1.90	2.668 (4)	150
O22—H22O···O16	0.84	1.99	2.762 (3)	152
O23A—H23O···O20	0.98	1.82	2.646 (8)	140

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

The asymmetric unit contains two crystallographically independent molecules together with five methanol molecules. One of the methanol molecules is disordered over two sites, with occupancies refined and then fixed at 0.5. In general, the non-H atom sites were modelled with anisotropic displacement parameters and the partially occupied non-H sites were modelled with isotropic displacement parameters. A riding-atom model was used for the H atoms, with O—H distances of 0.84 Å and C—H distances in the range 0.98–1.00 Å, and with U_{iso}(H) = 1.2U_{eq}(C,O). The Freidel pairs were merged during the refinement and the absolute configuration was not determined.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal3.6* (Hall *et al.*, 1999), *ORTEPII* (Johnson, 1976) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*;

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