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(17*S*)-2*α*,3*α*,18*β*,23,24-Pentahydroxy-19(18→17)-*abeo*-28-norolean-12-en-21-one from the rhizome of *Phlomis umbrosa*

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A new nortriterpenoid, $C_{29}H_{48}O_6$, with a novel skeleton was isolated from the rhizome of *Phlomis umbrosa*. The compound is composed of a linear array of four fused six-membered rings and a five-membered ring. The central ring has a slightly distorted half-chair conformation, while the other three six-membered rings adopt chair conformations. There are one intra- and four intermolecular hydrogen bonds, forming an extensive hydrogen-bonding network within the crystal structure.

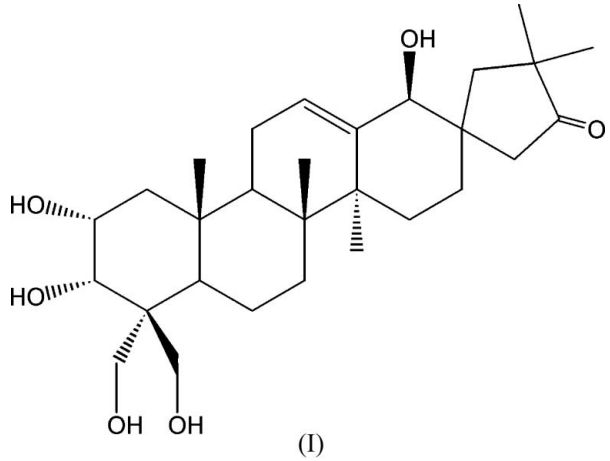
Key indicators

Single-crystal X-ray study
T = 294 K
Mean *σ*(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.119
Data-to-parameter ratio = 9.0

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

Comment

Phlomis umbrosa turcz is a perennial herbaceous plant growing in Hubei, Henan, Sichuan and Hebei provinces of China. Its rhizome, known as Si Lengma (Chinese name), has been used to treat colds, reduce swelling and staunch bleeding in traditional medicine (Fu *et al.*, 1999). In preliminary investigations of this plant, some triterpenoids (Zhao *et al.*, 1999), iridoid glycosides (Zhang *et al.*, 1991; Guo *et al.*, 2001) and phenylethanoid glycosides (Yang *et al.*, 2004) have been reported from this plant. To investigate bioactive natural products from *P. umbrosa*, chemical studies of its rhizome have been undertaken. A novel nortriterpenoid, *viz*. (17*S*)-2*α*,3*α*,18*β*,23,24-pentahydroxy-19(18→17)-*abeo*-28-norolean-12-en-21-one, (I), was isolated from the petroleum ether extract. Its structure was elucidated by extensive spectroscopic analysis, including two-dimensional NMR spectroscopy, and confirmed by single-crystal X-ray diffraction analysis.



(I)

The title compound was obtained as colourless plates in the orthorhombic space group $P2_12_12_1$. The X-ray data allowed

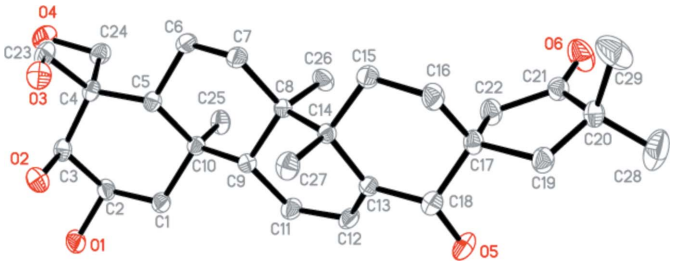


Figure 1
View of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

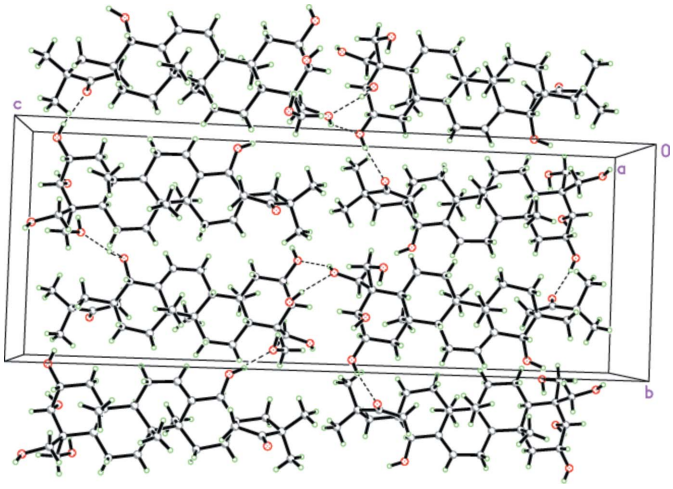


Figure 2
The crystal packing of (I), viewed along the *a* axis. Dashed lines indicate the hydrogen-bonding interactions.

determination of the relative stereochemistry of the molecules in the crystal studied; a view of the molecular structure of (I) with the numbering scheme is shown in Fig. 1 and selected dimensions are given in Table 1. The molecule is composed of four fused six-membered rings and a five-membered ring, *viz.* *A* (C1–C5/C10), *B* (C5–C10), *C* (C8/C9/C11–C14), *D* (C13/C14–C18) and *E* (C17/C19–C22). Rings *A*, *B* and *D* adopt chair conformations, while ring *C* adopts a slightly distorted half-chair conformation as a result of the double bond between atoms C12 and C13. Ring *E* adopts a half-chair conformation. Because of the spiro junction, atom C17 has a distorted tetrahedral geometry, with the C19—C17—C22 and C16—C17—C22 angles deviating significantly from ideal tetrahedral values. The C2—OH bond is equatorial and the C3—OH bond is axial. The hydroxy group attached to atom C18 in ring *D* is equatorial.

The hydroxy groups located at atoms C2, C3, C18, C23 and C24, and the carbonyl group located at atom C21 participate in hydrogen bonding. The six groups serve as hydrogen-bond donors and acceptors simultaneously (Table 2 and Fig. 2), resulting in four intermolecular O—H···O hydrogen bonds and one intramolecular hydrogen bond. These interactions form an extensive hydrogen-bonding network and further stabilize the crystal structure.

Experimental

The rhizome of *Phlomis umbrosa* turcz was collected in Hubei province, China, January 2005. The plants were identified by Professor Ding-Rong Wan, College of Life Sciences, South-Central University for Nationalities. A voucher specimen (D20050110) was deposited in the School of Pharmacy, Tinjing Medical University. The air-dried material (3400 g) of *P. umbrosa* was extracted three times with 95% ethanol under reflux. The 95% ethanol extract (500 g) was suspended in water, then extracted with petroleum ether, ethyl acetate and *n*-butanol successively. The petroleum ether layer (20 g) was chromatographed on a silica-gel column (400 g) eluted with a petroleum ether–EtOAc system with increased polarity to give 18 fractions. Fraction 13 was further separated on Toyopear HW-40 and then by HPLC–ODS to afford 0.045 g of the title compound, (I) (m.p. 562.5–563.5 K). ^{13}C NMR (300 MHz, C_5ND_5): δ 43.8 (C1), 66.8 (C2), 74.2 (C3), 48.0 (C4), 45.3 (C5), 19.4 (C6), 35.1 (C7), 40.2 (C8), 48.4 (C9), 38.7 (C10), 23.9 (C11), 119.8 (C12), 142.6 (C13), 44.5 (C14), 28.2 (C15), 36.0 (C16), 43.6 (C17), 75.4 (C18), 50.9 (C19), 45.6 (C20), 222.4 (C21), 41.7 (C22), 64.6 (C23), 69.6 (C24), 17.8 (C25), 18.1 (C26), 23.4 (C27), 26.0 (C28), 29.4 (C29). Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution at room temperature.

Crystal data

$C_{29}H_{46}O_6$
M_r = 490.66
Orthorhombic, $P2_12_12_1$
a = 7.0637 (10) Å
b = 11.6334 (17) Å
c = 31.080 (4) Å
V = 2554.0 (6) Å^3
Z = 4
D_x = 1.276 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2980 reflections
θ = 2.6–22.2°
μ = 0.09 mm^{-1}
T = 294 (2) K
Plate, colourless
0.22 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.981, T_{max} = 0.993
14539 measured reflections
3012 independent reflections
2090 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 26.4°
$h = -8 \rightarrow 4$
$k = -14 \rightarrow 14$
$l = -38 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.119
S = 1.03
3012 reflections
336 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.437 (4)	O4—C24	1.432 (4)
O2—C3	1.439 (4)	O5—C18	1.430 (4)
O3—C23	1.426 (4)		
C16—C17—C22	114.3 (3)	C22—C17—C19	103.4 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6^{i}	0.77 (5)	2.21 (5)	2.957 (4)	165 (5)
O2—H2···O4^{ii}	0.86 (4)	1.99 (4)	2.818 (4)	161 (4)
O3—H3···O2	0.86 (4)	1.93 (4)	2.663 (4)	142 (4)
O4—H4···O1^{iii}	0.79 (4)	2.09 (4)	2.755 (4)	142 (4)
O5—H5···O3^{iv}	0.94 (4)	1.88 (4)	2.797 (3)	167 (4)

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

Hydroxy atoms H1, H2, H3, H4 and H5 were located in a difference map and refined with distance restraints [U_{iso}(H) = 1.5U_{eq}(O)] on their bonds to atoms O1, O2, O3, O4 and O5, respectively. Other H atoms were positioned geometrically and refined as riding (C—H = 0.93–0.98 Å). For the CH and CH_2 groups, U_{iso}(H) values were set equal to 1.2U_{eq}(C), and for the methyl groups they were set equal to 1.5U_{eq}(C). The absolute configuration could not be established because of the absence of significant anomalous effects. Friedel pairs were merged for the final cycles of refinement.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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