Juan Zou, Tian-Tian Tang, Jiang-Hai Ye, Chen-Liang Zhao, Kang He and Lu-Tai Pan*
Crystal structure of 6-hydroxy-4,8,11b-trimethyltetradecahydro-8,11-epoxy-6a,9-methanocyclohepta[a]naphthalene-4-carboxylic acid – methanol (1/1), C₂₀H₃₀O₄

<https://doi.org/10.1515/ncrs-2019-0075>

Received January 24, 2019; accepted March 19, 2019; available online April 22, 2019

Abstract

C₂₀H₃₀O₄, orthorhombic, *P*2₁2₁2 (no. 18), *a* = 12.6727(4) Å, *b* = 19.8422(7) Å, *c* = 7.5471(3) Å, *V* = 1897.75(12) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0448, *wR*_{ref}(*F*²) = 0.1311, *T* = 243(2) K.

CCDC no.: 1904094

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Lu-Tai Pan, Guizhou University of Traditional Chinese Medicine, Guiyang 550025, P.R. China, e-mail: ltpan@sina.cn

Juan Zou, Tian-Tian Tang, Jiang-Hai Ye, Chen-Liang Zhao and Kang He: Guizhou University of Traditional Chinese Medicine, Guiyang 550025, P.R. China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.21 × 0.24 × 0.22 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.085 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ _{max} , completeness:	28.3°, 99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	26739, 4690, 0.021
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4454
<i>N</i> (<i>param</i>) _{refined} :	249
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

The aerial part of *Pteris semipinnata* were collected and identified by Jun-hua Zhao, in October, 2016. After being crushed into powder (28 kg), the plant material was extracted with ethyl acetate and filtered. The solvent was then distilled off (residue, 380 g). The crude product was subjected to MCI GEL CHP20P (75~150 μm) in order to remove most of the chlorophyll and continuously divided into 5 fractions (A–E) after being subjected to silica gel column eluting with petroleum ether/ethyl acetate (90:10–1:1). Subsequently, fraction A (177 g) was separated by silica gel column, Sephadex LH-20 and semi-preparative HPLC (Agilent 1100) to afford the crude product (20 mg) which was then crystallized from methanol to yield the title compound as colorless crystals (10 mg).

Experimental details

Using Olex2 [2], the structure was solved using Charge Flipping and refined with the ShelXL [4] refinement. All hydrogen atoms were positioned geometrically, with the *d*(C–H) = 0.97–0.99 Å, *U*_{iso}(H) = 1.2 times *U*_{eq}(C) and *U*_{iso}(H) = 1.5 times *U*_{eq}(O). The solvent molecules are disordered.

Discussion

In traditional Chinese medicine (TCM), the whole parts of *Pteris semipinnata* were used as herbal medicines for hundreds of years to treat apoplexy, acesodyne, snake bites, diarrhea, jaundice and so on [5]. In addition, this plant has been studied for its significant antitumor activity for years [6–11]. In our continuous endeavor to search for structurally fascinating natural products from *Pteris semipinnata*,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.7259(3)	0.90111(14)	1.1488(4)	0.0493(7)
H1A	0.6714	0.9343	1.1254	0.074*
H1B	0.7938	0.9234	1.1572	0.074*
H1C	0.7107	0.8782	1.2595	0.074*
C2	0.72858(18)	0.85039(11)	1.0001(3)	0.0323(4)
C3	0.81630(18)	0.79723(11)	1.0081(3)	0.0294(4)
H3A	0.8000	0.7619	1.0945	0.035*
H3B	0.8846	0.8175	1.0373	0.035*
C4	0.81493(15)	0.76969(10)	0.8172(2)	0.0223(4)
C5	0.82460(18)	0.83783(11)	0.7189(3)	0.0307(4)
H5A	0.8938	0.8586	0.7384	0.037*
H5B	0.8127	0.8325	0.5913	0.037*
C6	0.7364(2)	0.87891(11)	0.8059(3)	0.0336(5)
H6	0.7483	0.9282	0.8011	0.040*
C7	0.63219(19)	0.85713(11)	0.7248(3)	0.0351(5)
H7A	0.6376	0.8511	0.5962	0.042*
H7B	0.5752	0.8889	0.7518	0.042*
C8	0.61789(17)	0.79011(11)	0.8213(3)	0.0294(4)
H8	0.5466	0.7712	0.8007	0.035*
C9	0.70454(14)	0.73665(10)	0.7884(2)	0.0215(3)
H9	0.6970	0.7046	0.8881	0.026*
C10	0.68906(14)	0.69241(10)	0.6188(3)	0.0224(4)
C11	0.78538(14)	0.64442(9)	0.6092(2)	0.0198(3)
H11	0.7869	0.6222	0.7266	0.024*
C12	0.88861(14)	0.68443(10)	0.6017(2)	0.0214(4)
H12A	0.9477	0.6536	0.5805	0.026*
H12B	0.8858	0.7167	0.5035	0.026*
C13	0.90589(14)	0.72194(10)	0.7751(2)	0.0230(4)
H13	0.9713	0.7489	0.7644	0.028*
C14	0.58834(16)	0.64937(12)	0.6491(4)	0.0362(5)
H14A	0.5912	0.6297	0.7681	0.043*
H14B	0.5264	0.6788	0.6438	0.043*
C15	0.57535(18)	0.59293(13)	0.5139(4)	0.0414(6)
H15A	0.5126	0.5663	0.5430	0.050*
H15B	0.5652	0.6124	0.3958	0.050*
C16	0.67188(19)	0.54724(11)	0.5122(4)	0.0368(5)
H16A	0.6621	0.5124	0.4218	0.044*
H16B	0.6776	0.5247	0.6274	0.044*
C17	0.77504(16)	0.58500(10)	0.4746(3)	0.0257(4)
C18	0.8673(2)	0.53526(11)	0.5020(4)	0.0369(5)
H18A	0.8736	0.5245	0.6269	0.055*
H18B	0.9324	0.5557	0.4609	0.055*
H18C	0.8540	0.4943	0.4353	0.055*
C19	0.78046(18)	0.60442(11)	0.2789(3)	0.0302(4)
C20	0.67435(17)	0.73293(12)	0.4469(3)	0.0302(4)
H20A	0.7363	0.7605	0.4260	0.045*
H20B	0.6128	0.7617	0.4578	0.045*
H20C	0.6646	0.7022	0.3483	0.045*
C21	0.5000	0.5000	1.0532(13)	0.102(2)
H21A ^a	0.4846	0.4859	1.1721	0.153*
H21B ^a	0.4386	0.5234	1.0110	0.153*
H21C ^a	0.4871	0.4523	1.0517	0.153*
O1	0.62980(13)	0.81309(8)	1.0024(2)	0.0332(4)
O2	0.7211(2)	0.58455(14)	0.1658(3)	0.0632(7)
O3	0.86163(13)	0.64361(9)	0.2409(2)	0.0348(4)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H3	0.8626	0.6513	0.1328	0.052*
O4	0.92025(12)	0.67354(9)	0.91505(19)	0.0307(3)
H4	0.9858(18)	0.6677(16)	0.930(5)	0.046(9)*
O6 ^b	0.5193(15)	0.5643(8)	1.018(3)	0.124(6)
H6A ^b	0.5816	0.5731	1.0418	0.187*
O6A ^b	0.5810(13)	0.5097(11)	0.962(2)	0.116(6)
H6AA ^b	0.5599	0.5326	0.8555	0.174*

^aOccupancy: 0.5, ^bOccupancy: 0.25.

the title compound was found. The compound is a diterpene possessing a 6/6/6/5 carbon ring system. The two six-membered rings A (atoms C10, C11, C14–C17), B (atoms C4, C9–C13) and C (atoms C4–C9) are in chair conformations. In addition, the five-membered carbon ring (atoms C2–C6) shows an envelope conformation on C4. This structure also contains one hydroxyl group, one carboxyl group, one oxygen bridge and three methyl groups. These functional groups were identified by the distances $d(\text{C2}–\text{O1}) = 1.454(3)$ Å, $d(\text{C8}–\text{O1}) = 1.449(3)$ Å, $d(\text{C19}–\text{O2}) = 1.321(3)$ Å, $d(\text{C19}–\text{O3}) = 1.204(3)$ Å, $d(\text{C13}–\text{O4}) = 1.439(2)$ Å, respectively. The bond distances and bond angles in the title structure are all in expected ranges. The intermolecular connection was achieved through non-classical hydrogen bonds.

Acknowledgements: The authors gratefully acknowledge support from domestic first-rate fund of China [GNYL (2017)008], the Youth Science and Technology Talent Project of Guizhou Province [(2017)5618], the National Natural Science Foundation of China [81660723] and the Science and Technology Fund of Guizhou [(2013)2070].

References

1. BRUKER. SAINT, APEX2 and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
3. Sheldrick, G. M.: SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
5. He, T. P.; Wu, K. F.; Lu, Y. N.; Gong, X. L.; Chen, G. G.; Liang, N. C.: Effect of 5F from *Pteris semipinnata* on expression of Nr1d1 in HO-8910PM cell line. *China J. Chin. Mater. Med.* **34** (2009) 1268–1271.
6. Gong, X. L.; Chen, Z. H.; Liang, N. C.: Advances in study on chemical constituents and pharmacological activities of plants of genus *Pteris*. *China J. Chin. Mater. Med.* **32** (2007) 1382–1387.

7. Gong, X. L.; Chen, Z. H.; Liang, N. C.: Study on antitumor effect of extraction and compounds from *Pteris Semipinnata* L. J. Sichuan Trad. Chin. Med. **27** (2009) 51–53.
8. Gong, X. L.; Chen, Z. H.; Liang, N. C.; Deng, Y. F.: Isolation and identification of glycoside of compound 5F from *Pteris semipinnata* L. and their antitumor activity. Chin. Trad. Patent Med. **32** (2010) 257–260.
9. Li, L.; Chen, G. G.; Lu, Y. N.; Liu, Y.; Wu, K. F.; Gong, X. L.; Gou, Z. P.; Li, M. Y.; Liang, N. C.: Ent-11 α -hydroxy-15-oxo-kaur-16-en-19-oic-acid inhibits growth of human lung cancer A549 cells by arresting cell cycle and triggering apoptosis. Chin. J. Cancer Res. **24** (2012) 109–115.
10. Gong, X. L.; Liang, N. C.; Deng, Y. F.: Isolation and purification of an active antitumor compound 6F from *Pteris semipinnata* L. Asia-Pacific Trad. Med. **8** (2012) 29–30.
11. Qiu, M. S.; Yang, B.; Cao, D.; Zhu, J. P.; Jin, J.; Chen, Y. Y.; Zhou, L.; Luo, X.; Zhao, Z. X.: Two new hydroxylated ent-kauranoic acids from *Pteris semipinnata*. Phytochem. Lett. **16** (2016) 156–162.