



Natural Product Research

Formerly Natural Product Letters

ISSN: 1478-6419 (Print) 1478-6427 (Online) Journal homepage: <https://www.tandfonline.com/loi/gnpl20>


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To cite this article: Lei Sun, Hua-Ping Hu, Xiao-Xiao Chen, Guo-Yong Xu, Jin-Song Liu, Jiang-Miao Hu, De-Ling Wu & Feng-Qing Xu (2019): Two new acetoisovanillone glycosides from the water-soluble fraction of *Paeonia ostii*, Natural Product Research, DOI: [10.1080/14786419.2019.1687476](https://doi.org/10.1080/14786419.2019.1687476)

To link to this article: <https://doi.org/10.1080/14786419.2019.1687476>

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 Published online: 10 Nov 2019.

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Two new acetoisovanillone glycosides from the water-soluble fraction of *Paeonia ostii*

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ABSTRACT

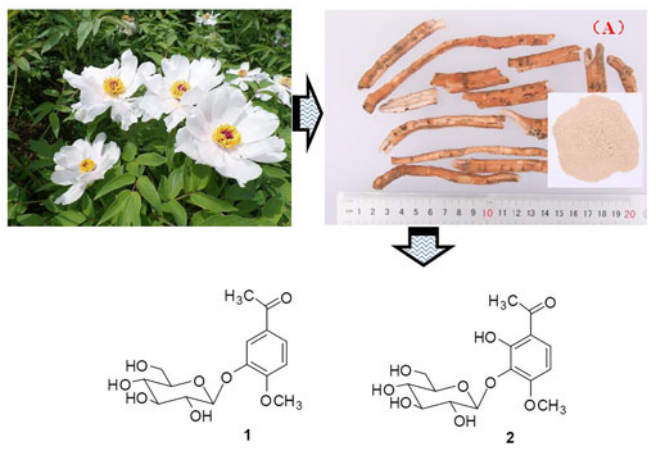
The cortex root of *Paeonia ostii*, is used as a traditional Chinese medicine for treating female diseases. Phytochemical investigation of the water-soluble fraction of the plant led to the isolation of two new acetoisovanillone glycosides: acetoisovanillone-3-O- β -D-glucopyranoside (**1**) and 2-hydroxy-acetoisovanillone-3-O- β -D-glucopyranoside (**2**). Their structures were elucidated by extensive spectroscopic methods.

ARTICLE HISTORY

Received 15 September 2019
Accepted 26 October 2019

KEYWORDS

Paeonia ostii T. Hong et J. X. Zhang; acetoisovanillone glycoside; water-soluble extraction




1. Introduction

The genus *Paeonia* comprises approximately 35 species, which are mainly distributed in the temperate regions of Asia and Europe, 15 species and hundreds of cultivars in

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 Supplemental data for this article can be accessed at <https://doi.org/10.1080/14786419.2019.1687476>.

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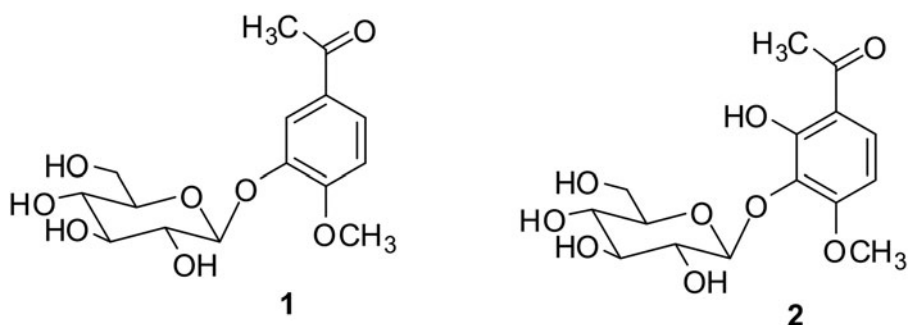


Figure 1. The structures of compounds 1–2.

China (Editorial Committee of Flora Reipublicae Popularis Sinicae 1979). Some species of Sect. Moutan DC. have been planted as ornamentals for their exotic flowers and their medicinal values (Li 1999). The genus led to the isolation of monoterpenoids, paeonols, tannins, stilbenes, flavonoids and their related glycosides (Wang et al. 2005; Song et al. 2014; Ogawa et al. 2015). The root cortex of Mudan, which is originated from *P. suffruticosa* and *P. ostii*, has been used as a folk medicine for removing heat from the blood and extravasating blood (Hong et al. 1992; Hong and Pan 1999; He et al. 2014), especially for gynecological disease (Li et al. 2009; Wang et al. 2017). *P. ostii*, it is cultivated in Tong-ling (Anhui Province) for medicinal uses for 500 years and well-known for its genuine features. In our previous phytochemical studies on endophytic fungus from the root cortex of *P. ostii*, we obtained globoscinic acid derivatives, pyridine derivatives, steroids and so on (Wang et al. 2018; Zhang et al. 2018, 2019). As part of our continuous study on the chemical constituents, we describe the isolation process and structural elucidation of the new derivatives of acetoisovanillone glycoside (1–2) from the water-soluble extraction of the root cortex of this plant in this paper.

2. Results and discussion

The ethanol extracts of *P. ostii* root-barks were successively partitioned with Pet, EtOAc, *n*-BuOH and H₂O. From the water-soluble fraction, two new compounds (Figure 1) and nine known ones were isolated. The known ones were identified as 4-methoxyl-paeoniflorin (3) (Braca et al. 2008), benzoylpaeoniflorin (4) and paeoniflorin (5) (Kaneda et al. 1972), 6'-*O*-vanillylpaeoniflorin (6) (An et al. 2006), lactiflorin (7) (Lang et al. 1990), albiflorin (8) (Kaneda et al. 1972), oxypaeoniflorin (9) (Ding et al. 2012), apiopaeonoside (10) (Yu et al. 1986), suffruticosides E (11) (Yoshikawa et al. 1992), based on comparison with NMR and MS data in the literature.

Compound 1 was obtained as a white amorphous powder and its molecular formula was determined to be C₁₅H₂₀O₈ from the negative ion HR-ESI-MS at *m/z* 363.0854 ([M + Cl]⁻, calcd for C₁₅H₂₀ClO₈, 363.0847) with six degrees of unsaturation. The infrared (IR) spectrum showed absorption bands at 1663, 1600, 1588 and 1519 cm⁻¹ suggestive of a benzene ring attached to the carbonyl group and a broad band at 3435 cm⁻¹ ascribable to hydroxyl groups. The ¹H NMR spectrum (Table S1) of 1 exhibited an ABX-system aromatic protons [δ_{H} 7.78 (1H, d, *J* = 2.4 Hz), 7.72 (1H, dd,

$J=8.4, 2.4\text{ Hz}$), 7.08 (1H, dd, $J=8.4\text{ Hz}$], a set of characteristic protons attached to oxygen-bearing carbons at δ_{H} 4.96 (d, $J=7.8\text{ Hz}$, H-1'), 3.50 (dd, $J=9.6, 7.8\text{ Hz}$, H-2'), 3.48 (t, $J=9.6\text{ Hz}$, H-3'), 3.39 (dd, $J=9.6, 8.4\text{ Hz}$, H-4'), 3.45 (ddd, $J=8.4, 6.0, 2.4$, H-5'), 3.90 (dd, $J=12.0, 2.4\text{ Hz}$, H-6'a), 3.70 (dd, $J=12.0, 6.0\text{ Hz}$, H-6'b) ascribable to a glucose moiety, as well as two singlet methyl signals [3.93, 2.55 (3H each, s)]. The ^{13}C NMR spectrum exhibited 15 resonances signals were assigned to a keto carbonyl group, an aromatic ring, two methyl groups and a hexose unit, implying **1** is a derivative of acetophenone glycoside. Detailed comparison of the NMR spectroscopic data with those of androsin (Marty et al. 1996) revealed that they were similar. The slight difference of that the chemical shift of H-2 lower field than H-6 in **1** other than in androsin. The methoxyl group located at C-4 was determined by the expected HMBC correlations of H-6 (δ_{H} 7.72) to C-2 and C-4, from H-2 (δ_{H} 7.78) to C-3, C-4 and C-6, from the singlet proton signals at δ_{H} 3.93 to C-4. In addition, a long-range correlation from the anomeric proton signal at δ_{H} 4.96 ($J=7.8\text{ Hz}$) to the carbon signal at δ_{C} 146.4 indicated that the sugar moiety was attached to C-3 via a β -linkage. The HSQC and ^1H - ^1H COSY spectra (Figure S1) permitted the assignments of the hexosyl unit, which was confirmed to be a D-glc by the results of acid hydrolysis (Pan et al. 2011; Xu et al. 2018). Therefore, the structure of **1** was determined to be acetoisovanillone-3- O - β -D-glucopyranoside.

Compound **2** was obtained as a white amorphous powder. Its molecular formula of $\text{C}_{15}\text{H}_{20}\text{O}_9$ deduced from the negative ion HR-ESI-MS at m/z 343.1037 ($[\text{M} - \text{H}]^-$, calcd for $\text{C}_{15}\text{H}_{19}\text{O}_9$ 343.1029). The ^1H NMR spectrum (Table S1) of **1** exhibited an AX-system aromatic protons [δ_{H} 7.71 (1H, d, $J=9.0\text{ Hz}$), 6.68 (1H, d, $J=9.0\text{ Hz}$], an anomeric proton signal at δ_{H} 4.93 (1H, d, $J=7.8\text{ Hz}$) as well as two singlet methyl signals at 3.93 and 2.59 (3H each, s). Compared with **1**, the NMR spectroscopic properties were similar (Table S1) except that one aromatic proton was omitted in **2**, and C-2 signal was downfield by 29.5 ppm, while those of C-1, C-3 and C-5 were upfield by 14.9, 13.6 and 7.8 ppm, respectively. Considering the above data, a hydroxyl group should be attached to C-2. Furthermore, the expected correlations (Figure 1) of H-6 to C-1, C-4 and C-7, of H-5 to C-1 and C-3 in the HMBC spectra, correlations of H-5/H-6 in ^1H - ^1H COSY spectra. Others assignments listed were based on 2D NMR correlations. Thus, compound **2** was identified as 2-hydroxy-acetoisovanillone-3- O - β -D-glucopyranoside.

3. Conclusion

Chemical investigation of the root cortex of *P. ostii* resulted in isolation of two new acetoisovanillone glycosides (**1–2**), along with known compounds including six monoterpene glycosides possessing a “cage-like” pinane skeleton (**3–8**) and three phenolic glycosides (**9–11**). Compounds **3**, **6–8** and **11** were originally obtained from this plant.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This project was financially supported by the Open Fund of State Key Laboratory of Phytochemistry and Plant Resources in West China (P2017-KF03) and Anhui Innovative Team from Colleges for Scientific Research's Platform-The Innovative Team in Researching the Key Technologies concerning the Integration of Processing Chinese Medicine Decoction Pieces in Producing Area; We also thank the analytical group of the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences and Department of Material Science and Information Technology, Anhui University, for spectra test.

References

- An RB, Kim HC, Lee SH, Jeong GS, Sohn DH, Park H, Kwon DY, Lee JH, Kim YC. 2006. A new monoterpene glycoside and antibacterial monoterpene glycosides from *Paeonia suffruticosa*. *Arch Pharm Res.* 29(10):815–820.
- Braca A, Kiem PV, Yen PH, Nhiem NX, Quang TH, Cuong NX, Minh CV. 2008. New monoterpene glycosides from *Paeonia lactiflora*. *Fitoterapia.* 79(2):117–120.
- Ding LQ, Zhao F, Chen LX, Jiang ZH, Liu Y, Li ZM, Qiu F, Yao XS. 2012. New monoterpene glycosides from *Paeonia suffruticosa* Andrews and their inhibition on NO production in LPS-induced RAW 264.7 cells. *Bioorg Med Chem Lett.* 22(23):7243–7247.
- Editorial Committee of Flora Reipublicae Popularis Sinicae. 1979. *Flora Reipublicae Popularis Sinicae*. Vol. 27. Beijing, China: Academic Press; p. 37–59.
- He CN, Peng B, Dan Y, Peng Y, Xiao PG. 2014. Chemical taxonomy of tree peony species from china based on root cortex metabolic fingerprinting. *Phytochemistry.* 107:69–79.
- Hong DY, Pan KY. 1999. Taxonomical history and revision of *Paeonia* sect. *Moutan* (Paeoniaceae). *Acta Phytotaxon Sin.* 37:351–368.
- Hong T, Zhang JX, Li JY, Zhao WZ, Li MR. 1992. Study on the Chinese woody peonies (I) New Taxa of *Paeonia* L. Sect. *Moutan* DC. *Bull Bot Res.* 12:223–234.
- Kaneda M, Iitaka Y, Shibata S. 1972. Chemical studies on the oriental plant drugs-XXXIII. The absolute structures of paeoniflorin, arbutiflorin, oxypaeoniflorin and benzoylpaeoniflorin isolated from Chinese peony root. *Tetrahedron.* 28(16):4309–4317.
- Lang HY, Li SZ, Wang HB, Yu DQ, Liang XT. 1990. The structure of lactiflorin, an artifact during isolation? *Tetrahedron.* 46:3123–3128.
- Li CH, Du H, Wang LS, Shu QY, Zheng YR, Xu YJ, Zhang JJ, Zhang J, Yang RZ, Ge YX. 2009. Flavonoid composition and antioxidant activity of tree peony (*Paeonia* section *Moutan*) yellow flowers. *J Agric Food Chem.* 57(18):8496–8503.
- Li JJ. 1999. *Chinese tree and herbaceous peonies*. Beijing, China: China Forestry Publishing House; p. 1–200.
- Marty D, Gillet-Manceau F, Fliniaux MA, Jacquin-Dubreuil A, Monti JP. 1996. Two-dimensional NMR identification of an acetophenone glycoside isolated from solanaceous cell suspensions. *Spectrosc Lett.* 129:169–174.
- Ogawa K, Nakamura S, Sugimoto S, Tsukioka J, Hinomaru F, Nakashima S, Matsumoto T, Ohta T, Fujimoto K, Yoshikawa M, et al. 2015. Constituents of flowers of Paeoniaceae plants, *Paeonia suffruticosa* and *Paeonia lactiflora*. *Phytochem Lett.* 12:98–104.
- Pan LL, Fang PL, Zhang XJ, Ni W, Li L, Yang LM, Chen CX, Zheng YT, Li CT, Hao XJ, et al. 2011. Tiglane-type diterpenoid glycosides from *Euphorbia fischeriana*. *J Nat Prod.* 74(6):1508–1512.
- Song WH, Cheng ZH, Chen DF. 2014. Anticomplement monoterpene glycosides from the root bark of *Paeonia suffruticosa*. *J Nat Prod.* 77(1):42–48.
- Wang JT, Zhang PL, Liu JS, Wang GK, Xu FQ, Chen L, Yu Y, Wang G. 2018. Aspergillates A to E, second metabolites from *Aspergillus* sp. isolated from *Paeonia ostii*. *Fitoterapia.* 131:204–208.

- Wang X, Cheng CG, Sun QL, Li FW, Liu JH, Zheng CC. 2005. Isolation and purification of four flavonoid constituents from the flowers of *Paeonia suffruticosa* by high-speed counter-current chromatography. *J Chromatogr A*. 1075(1–2):127–131.
- Wang Z, He C, Peng Y, Chen F, Xiao P. 2017. Phytochemistry, pharmacology, analytical methods and safety of cortex moutan (*Paeonia suffruticosa* Andrew): a systematic review. *Molecules*. 22(6):946–972.
- Xu FQ, Fan WW, Zi CT, Zhou J, Hu JM. 2018. Three new glycosides from the stems and leaves of *Passiflora edulis*. *Chin J Org Chem*. 38(2):526–530.
- Yoshikawa M, Uchida E, Kawaguchi A, Kitagawa I, Yamahara J. 1992. Galloyl-oxypaeoniflorin, suffruticosides A, B, C, and D, five new antioxidative glycosides, and suffruticoside E, A paeonol glycoside, from Chinese moutan cortex. *Chem Pharm Bull*. 40(8):2248–2250.
- Yu J, Lang HY, Xiao PG. 1986. A new compound, apiopaeonoside, isolated from the root of *Paeonia suffruticosa*. *Acta Pharm Sin*. 21:191–197.
- Zhang PL, Wang G, Liu JS, Xu FQ, Zhao ZZ, Wang WX, Wang JT, Wang GK, Wu PY. 2018. Three new metabolites from the endophytic fungus *Climacocystis montana* isolated from the root bark of *Paeonia ostia*. *Phytochem Lett*. 26:50–54.
- Zhang PL, Wang G, Xu FQ, Liu JS, Wang JT, Zhang R, Liu HT, Hu JM, Wang GK, Wu PY. 2019. Aspergilolide, a steroid lactone produced by an endophytic fungus *Aspergillus* sp. MBL1612 isolated from *Paeonia ostii*. *Nat Prod Res*. 33(15):2133–2138.