A new cycloartane triterpenoid from the leaves and stems of *Fritillaria hupehensis*

Hui Fang Pi, Peng Zhang, Tian Zhu, Han Li Ruan, Yong Hui Zhang, Han Dong Sun, Ji Zhou Wu

*Faculty of Pharmaceutical Sciences, Tongji Medical College of Huazhong University of Science and Technology, Wuhan 430030, China*
*State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Kunming 650204, China*

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Abstract

A new triterpenoid has been isolated from the leaves and stems of *Fritillaria hupehensis* Hsiao et K.C. Hsia. Its structure was established as (23Z)-9,19-cycloart-23-ene-3α,25-diol 1 through chemical and spectroscopic studies including 2D NMR. Another known triterpenoid 9,19-cycloart-25-ene-3β,24δ-diol 2 was also isolated.

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*Fritillaria hupehensis* Hsiao et K.C. Hsia, is a liliaceous plant growing in the southwest district of Hubei Province, China. Its bulbs have been recorded in Pharmacopoeia of the People’s Republic of China as a principal Chinese traditional medicine named “Hubeibaimu”, *ent*-kaurane diterpenoids and *C-nor-D-homo* steroidal alkaloids were isolated from the bulbs [1], but the chemical constituents of the leaves and stems of *F. hupehensis* have not been studied before. In our study, two cycloartane triterpenoids were isolated from the leaves and stems of the plant. The paper describes the isolation and structural elucidation of the new cycloartane triterpenoid (23Z)-9,19-cycloart-23-ene-3α,25-diol 1, along with the known triterpenoid 9,19-cycloart-25-ene-3β,24δ-diol 2, which has been isolated for the first time from this genus.

Compound 1 was obtained as colorless needles (Petroleum-EtOAc), mp 210–213 °C. Liebermann–Burchard reaction was positive. 1 showed [M]⁺ peak at m/z 442 in the FABMS corresponding to the molecular formula of C₃₀H₄₀O₂. The IR spectrum showed the presence of hydroxyl groups (3315 cm⁻¹). The ¹H NMR spectrum of 1 displayed two upfield shifted doublets at δ 0.55, 0.31 (d, J = 4.0 Hz) assignable to a cyclo-propyl methylene group (H₁-19) characteristic of cycloartane-type triterpenoids [2]. The spectrum also showed signals due to six methyl signals at δ 0.89 (s, 3H, H-28), 1.00 (s, 3H, H-18), 1.11 (s, 3H, H-29), 1.23 (s, 3H, H-30), 1.32 (s, 6H, H-26, 27) and one secondary methyl signal at δ 0.96 (d, 3H, J = 6.3 Hz, H-21), a signal due to the proton attached to the carbon-bearing oxygen at δ 3.47 (br. s), an olefinic signal at δ 5.96 (m, 2H, W₁/₂ = 8 Hz). The configuration of the double bond was assigned as Z, since the olefinic protons signal appeared as narrow multiplets with half bandwidth of 8 Hz [3].
signal at δ 1.32 was indicated the presence of an α-hydroxy isopropyl moiety, so the hydroxyl located at C-25. The broad singlet at δ 3.47 is characteristic of the proton geminal to the 3α-axial hydroxyl in cycloartanes [4]. The $^{13}$C NMR spectrum of 1 showed 30 carbon atoms (Table 1). The multiplicity assignments were made by 2D NMR and DEPT experiments. The HMBC experiment showed long-range correlations between the carbon signal at δ$_C$ 77.9 (C-3) and the proton signals at δ$_H$ 1.23 (H-2β), 1.32 (H-5), 1.11 (H-29) and δ$_C$ 124.5 (C-23), 141.6 (C-24) with the proton signals at δ$_H$ 2.29 (H-22), 1.32 (H-26, 27). The position of the double bond at C-23 was also confirmed by $^1$H-$^1$HCOSY spectroscopy, which showed the correlation of H-23, H-24 (δ$_H$ 5.96) to H-22 (δ$_H$ 1.89, 2.29). On the basis of the above evidence, the structure of 1 was determined to be (23Z)-9,19-cycloart-23-ene-3α,25-diol (Fig. 1).

![Fig. 1. The structures of compounds 1 and 2.](image-url)
The physical and spectral data of compound 2 were identical with those reported in the literature [5].

References