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Studies on the chemical constituents of *Valeriana fauriei* Briq

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Nine compounds were isolated from the roots of *Valeriana fauriei* Briq, of which one is a new germacrane-type sesquiterpenoid named as valerianin E and its structure was elucidated as bicyclo[8, 1, 0] 5 β -hydroxyl-7 β -acetoxy-5 α ,11, 11'-trimethyl-E-1(10)-ene-4 α , 15-olide (**1**). In addition, two were first reported from this genus and the others were isolated for the first time from the title plant.

Keywords: *Valeriana fauriei*; *Valeriana*; Germacrane; Valerianin; Sesquiterpenoid

1. Introduction

The roots of *Valeriana officinalis* L have been used in northwestern Europe as a mild sedative agent for hundreds of years and are still contenting in the Pharmacopoeias of Germany, England, Holland and Japan. *Valeriana fauriei* grows in northeast China and has been used for hundreds of years in Chinese medicine. But its chemical constituents have not been investigated [1]. In order to exploit its resources and provide chemotaxonomy information, a new sesquiterpenoid (**1**) together with eight known components were isolated. This paper deals with the isolation and structure elucidation of the new compound.

2. Results and discussion

Compound **1**, white powder, mp. 208–210°C. The molecular formula of C₁₇H₂₄O₅ for **1** was clarified by HR-MS, EI-MS and ¹³C-NMR spectra. The ¹³C-NMR signals at δ 169.9 and 21.2 indicated the presence of an acetyl group in compound **1**. A strong UV absorption at 249 nm together with an IR band at 1728 cm⁻¹ and a carbonyl signal at δ 171.9 in the ¹³C-NMR spectrum as well as NMR analysis were indicative of an α,β -unsaturated lactone.

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The ^{13}C -NMR spectrum exhibited 17 carbon signals. The DEPT experiment suggested 4 methyls, 3 methenes, 5 methines and 5 quaternary carbons. Further NMR spectrum exhibited signals typical for germacrane-type compound represented by **1**, the assignments of which are summarized in table 1.

The structure of **1** was further confirmed by the interpretation of 2D-NMR spectra. In the ^1H - ^1H COSY spectrum of **1**, two sets of coupling systems interrupted by C-5 were observed, one set of couplings was composed of H-2 and H-3, H-3 and H-4, and another set of couplings encompassed H-6 and H-7, H-7 and H-8, H-8 and H-9 as well as H-9 and H-10. In the HMBC spectrum a methyl proton signal at δ 1.12 showed long-range correlations with δ 62.5 (C-4), 58.1 (C-5) and 46.5 (C-6). So this methyl signal can be assignable to the proton of C-14. The HMBC spectrum also revealed long-range correlations as shown in figure 2. So the acetoxy group should be linked to C-6 and an isopropylidene was fused to C-8 and C-9 of the germacrane skeleton.

The relative configurations of C-4, C-5, C-7, C-8 and C-9 were deduced by comparison of the observed coupling constants with those from dihedralangles in Dreiding models and NOESY spectrum of **1**. The isopropylidene group was suggested to be *cis*-fused to the C-8 and C-9 of the parent framework. The orientation of H-8 was tentatively regarded as β and the coupling constant between H-8 and H-9 (11 Hz) indicated H-9 is *cis* to H-8 [2,3]. This fact was also confirmed by the observation of NOE correlation between H-8 and H-9 in the NOESY spectrum of **1**. The large coupling constant between H-7 and H-8 (11.5 Hz) showed clearly that H-7 is *trans* to H-8, indicating acetoxy group is oriented as β . The configurations of C-4 and C-5 were also elucidated by the interpretation of NOESY spectrum of **1**. The NOE correlations were observed between the signals of H-7 and 14- CH_3 , 9 β -H and H-4; there was no NOE correlation between H-4 and 14- CH_3 . So the orientations of 14- CH_3 and 4-H were favored to be α and β , respectively. The *E* type of isomerism around the C-1 and C-10 double bond was evident from NOE correlations between H-10 and 14- CH_3 and H-7. Thus the structure of **1** was elucidated as bicyclo[8, 10, 0]5 β -hydroxyl-7 β -acetoxy-5 α ,11, 11'-trimethyl-E-1(10)-ene-4 α , 15-olide (**1**). It is a new compound named as valerianin E.

Table 1. ^1H -NMR and ^{13}C -NMR data of compound **1**.

Carbon no.	δC	δH
1	132.4	
2	22.8	2.74 (1H, dt, $J = 13.5, 3$ Hz)
3	27.7	2.53 (1H, td, $J = 13.5, 3.5$ Hz) 2.25 (1H, m) 1.43 (1H, m)
4	62.5	2.95 (1H, dd, $J = 11.0, 2.0$)
5	58.1	
6	46.5	2.31 (1H, dd, $J = 12.5, 2.0$ Hz) 1.36 (1H, dd, $J = 12.5, 12$ Hz) 4.58 (1H, td, $J = 11.5, 2.0$ Hz)
7	70.2	1.27 (1H, dd, $J = 11.5, 11$ Hz)
8	39.4	1.73 (1H, dd, $J = 11, 9.0$ Hz)
9	28.7	6.97 (1H, d, $J = 9.0$ Hz)
10	143.0	
11	23.8	
12	28.2	1.19 (3H, s)
13	15.6	1.19 (3H, s)
14	17.6	1.12 (3H, s)
15	171.9	
16	169.9	
17	21.2	2.05 (3H, s)

The other compounds were identified as *p*-hydroxybenzoic acid methylate (**2**), *p*-anisic acid (**3**), Benzoic acid methylate (**4**), *o*-anisic acid (**5**), 7, 3', 4'-trimethoxyl quercetin (**6**) [4], 3 β , 15, 16, 19-tetrahydroxy-ent-pimar-7-ene (**7**), Quercetin (**8**) [5], Kaemferol (**9**) [6]. Among them **6** and **7** were first reported from this genus and the others were isolated for the first time from the title plant.

3. Experimental

3.1 General experimental procedures

Melting points were measured on a microscope melting point apparatus (Yanaco) and are uncorrected. UV spectra were obtained on a Shimadzu UV-260 spectrophotometer in EtOH solutions. IR spectra were recorded on a Bruker IR-27G. Mass spectra were recorded with VG7070E mass spectrometer. NMR spectra along with 2D-NMR were taken on an Inova-500 in CDCl₃. The $[\alpha]_D$ was recorded at 589 nm on a JASCO P-1020 spectrometer (cell length 100 mm). Silica gel was produced by Qingdao Factory of Marine Chemical Industry and the solvents used are analytical grade.

3.2 Plant material

The air-dried roots of *Valeriana fauriei*, collected in Liaoning province, China in October 1998, were identified by Professor Liu-Ke. A voucher specimen has been deposited at the Department of Traditional Chinese Medicine, Liaoning College of Traditional Chinese Medicine.

3.3 Extraction and isolation

The roots of *Valeriana fauriei* (2.0 Kg) were percolated with 20 times of MeOH under N₂ atmosphere and concentrated *in vacuo* to yield 200 g of MeOH extract, which was suspended in water and partitioned with hexane, CHCl₃ and EtOAc, respectively, to give hexane extract (30 g), CHCl₃ extract (17.5 g) and EtOAc extract (13 g).

The hexane extract was subjected to chromatography on silica gel column (1 kg) and eluted in a stepwise manner with hexane–ether mixture (9:1, 7:3, 6:4, 3:7) to give four fractions.

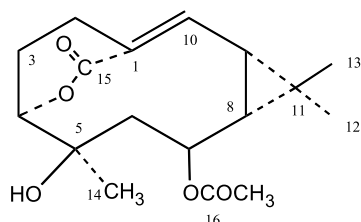
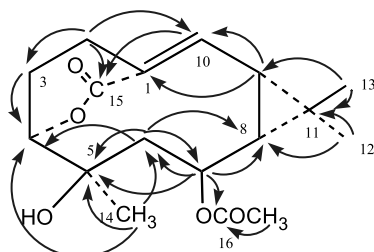
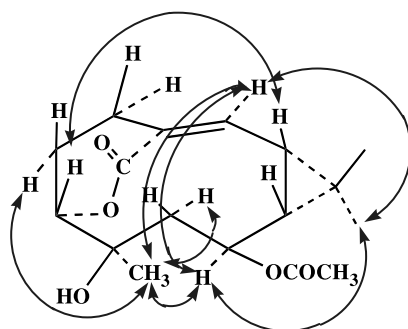
Repeated chromatography on silica gel column of fraction 1 (5 g) eluted with hexane–EtOAc and hexane–CHCl₃ to yield compound **1** (38 mg); repeated chromatography of fraction 2 (8 g) in a similar way to yield **2** (11 mg), **3** (2.6 mg), **4** (2.5 mg), **5** (2.5 mg).

The EtOAc extract was chromatographed on silica gel and eluted with CHCl₃–MeOH mixtures (20:1, 15:1, 10:1, 5:1) to afford five fractions.

Rechromatography of fraction 4 (2 g) on silica gel eluted with hexane–EtOAc and further purified by Sephadex LH-20 provided compounds **6** (3.5 mg), **7** (2.8 mg), **8** (4.5 mg) and **9** (3.0 mg).

3.4 Identification

Valerianin E (**1**) white powder, mp. 208–210°C. $[\alpha]_D - 36$ ($c = 0.1$, EtOH). IR (cm⁻¹): 3182 (br.), 2946 (m), 1728 (s), 1630 (w), 1371 (m), 1240 (s), 772 (m), 612 (w). HRSI-MS m/z ,

Figure 1. The structure of compound **1**.Figure 2. Key HMBC correlations of **1**.Figure 3. Key NOE correlations of **1**.

309.1691 $[M + H]^+$ (calcd for $C_{17}H_{24}O_5$, 309.1704) EI-MS m/z 308 (M^+ , 20), 43 (100). 1H -NMR and ^{13}C -NMR data are given in table 1.

Compounds **2** (*p*-hydroxybenzoic acid methylate), **3** (*p*-anisic acid), **4** (Benzoic acid methylate), **5** (*o*-anisic acid), **6** (7, 3', 4'-trimethoxyl quercetin), **7** (3 β , 15, 16, 19-tetrahydroxy-entpimar-7-ene), **8** (Quercetin), **9** (Kaemferol) were identified on the basis of 1H -NMR and ^{13}C -NMR spectra and EI-MS spectrum compared with those in references. figures 1–3

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