24-Hydroxyoleanane-Type Triterpenes from the Aerial Parts and Roots of *Oxytropis falcata*

Wen-Hao Chen,[†] Huan-Yang Qi,[‡] and Yan-Ping Shi*[,†,‡]

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China, and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

Received March 31, 2009

Phytochemical investigation of the aerial parts of *Oxytropis falcata* led to the isolation of three new 24-hydroxyoleanane-type triterpenes (**1**−**3**), seven known analogues (**4**−**10**), and two rare sesquiterpenoids (**12**, **13**). Compounds **6** and **12** were isolated as new natural products. Triterpenes (**5**, **6**, **8**, **11**) were isolated from the roots of *O. falcata*. The structures and relative configurations of these compounds were elucidated by spectroscopic analyses, including 1D and 2D NMR spectroscopy and mass spectrometry, and by comparison of their NMR data with those of related compounds. Single-crystal X-ray diffraction analyses confirmed the structures of **1**−**4**, and the absolute configuration of **3** was evidenced by the incorporation of DMSO (crystallization solvent) in the crystal lattice.

Plants of the genera *Astragalus* and *Oxytropis* containing the indolizidine alkaloid swainsonine are commonly known as locoweeds. These plants cause severe livestock poisoning and thus significant economic losses all over the world. A recent comprehensive review described the therapeutic potential for the toxic components of poisonous plants that belong to these genera.[1]

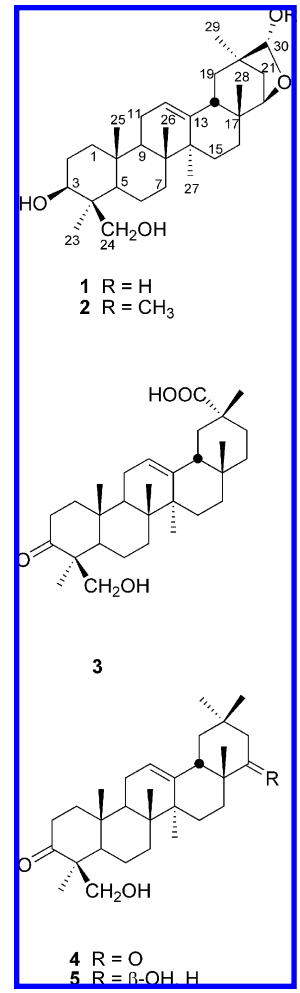
Oxytropis falcata Bunge (Leguminosae), known as a toxic plant, is a perennial herb that grows 1−35 cm high. Widely distributed in the west of China, it is commonly regarded as "the king of herbal medicine" in Tibetan medicine. Alcohol extracts of *O. falcata* mixed with other medicinal materials (Qingpenggao) have been patented as a treatment for pain and arthritis.[2]

In the course of our investigation of secondary metabolites produced by this poisonous plant, we recently described the isolation and crystal structure characterization of pendulone from the roots of *O. falcata.*[3] Pendulone exhibited remarkable in vitro antileishmanical activity with an IC_{50} value of 0.07 μg/mL.[4] Further investigations on the aerial parts and roots of *O. falcata* have resulted in the isolation and structure elucidation of three new 24-hydroxyoleanane-type triterpenoids, falcatins A (**1**) and B (**2**) and 3-oxo-azukisapogenol (**3**). Ten known compounds (**4**−**13**) were also isolated; two of them (**6**, **12**) were new natural products (structures of compounds **6**−**13** are included in the Supporting Information).

Results and Discussion

A 95% ethanol extract of the aerial parts of *O. falcata* was suspended in water and then partitioned successively with petroleum ether (60−90 °C), EtOAc, and *n*-BuOH. Column chromatography (CC) of the EtOAc-soluble fraction yielded compounds **1**−**10**, **12**, and **13**. The same procedure used on the roots of *O. falcata* yielded four known compounds (**5**, **6**, **8**, and **11**), of which only **11** was different from those isolated from the aerial parts.

Falcatin A (**1**) was isolated as colorless needles. Its HRESIMS displayed a pseudomolecular ion peak at *m/z* 495.3446 $[M + Na]^+$, suggesting the molecular formula $C_{30}H_{48}O_4$ and seven degrees of unsaturation. Fragment ions at *m/z* 454 $[M - H_2O]^+$ and *m/z* 436 $[M - 2H_2O]^+$ in the EIMS as well as an absorption band at 3376 cm^{-1} in the IR spectrum indicated the presence of at least two OH groups. The IR spectrum also showed absorption bands at 1118, 1090, and 1045 cm^{-1}, consistent with the presence of a C−O−C group.[5]



Strong evidence for an olean-12-ene derivative was observed in the EIMS of **1**. A retro-Diels−Alder (RDA) fragmentation is characteristic of the oleanene skeleton, where the D/E ring fragment maintains a positive charge at *m/z* 248 (92%). The A/B ring fragment also maintains a positive charge at *m/z* 224 (16%), but is less abundant.[6,7] The ^1H and ^{13}C NMR spectra of **1** were consistent with an olean-12-ene.[8−10] The ^{13}C NMR (Table 1) spectrum of **1** showed 30 signals, which by DEPT experiment revealed the presence of six sp^3 carbons (δ 16.3, 17.2, 21.1, 23.6, 23.9, and 25.4), two sp^2 olefinic carbons (δ 123.6 and 142.8), three oxyme-

* To whom correspondence should be addressed. Tel: +86-931-4968208. Fax: +86-931-8277088. E-mail: shiyp@lzb.ac.cn.
[†] Lanzhou University.
[‡] Lanzhou Institute of Chemical Physics.

10.1021/np900199x CCC: $40.75
Published on Web 07/28/2009

Table 1. ^{13}C NMR Spectroscopic Data (δ) of Compounds **1**−**3**[a]

C	**1**[b]	**2**[c]	**3**[b]
1	38.8 t	38.3 t	40.6 t
2	27.9 t	27.6 t	35.4 t
3	79.3 d	80.8 d	214.7 s
4	43.1 s	42.7 s	54.9 s
5	56.1 d	55.8 d	57.7 d
6	19.3 t	18.4 t	19.9 t
7	33.6 t	33.1 t	33.0 t
8	39.7 s	39.4 s	40.1 s
9	47.8 d	47.6 d	47.3 d
10	37.1 s	36.9 s	37.0 s
11	23.9 t	23.7 t	24.0 t
12	123.6 d	123.4 d	122.7 d
13	142.8 s	142.2 s	144.6 s
14	42.8 s	42.6 s	41.9 s
15	25.6 t	25.2 t	26.3 t
16	26.0 t	26.0 t	27.0 t
17	37.1 s	36.7 s	32.7 s
18	44.4 d	44.1 d	46.1 d
19	44.6 t	44.3 t	40.9 t
20	42.8 s	43.2 s	42.2 s
21	35.1 t	35.3 t	29.4 t
22	84.6 d	85.7 d	36.0 t
23	23.6 q	22.4 q	20.5 q
24	63.7 t	64.5 t	64.4 t
25	16.3 q	16.1 q	16.0 q
26	17.2 q	16.7 q	17.1 q
27	25.4 q	25.0 q	26.3 q
28	23.9 q	23.3 q	28.5 q
29	21.1 q	20.0 q	180.2 s
30	100.4 d	107.5 d	19.8 q
OCH_3		55.3 q	

[a] C-multiplicities were determined by DEPT135 data. [b] Spectra recorded at 75 MHz in DMSO-d_6. [c] Spectra recorded at 100 MHz in $CDCl_3$.

thine carbons (δ 79.3, 84.6, and 100.4), and one oxymethylene carbon (δ 63.7). The ^{1}H NMR spectrum revealed six tertiary methyl singlets [δ 0.76 (3H), 0.87 (3 × 3H), 1.07 (3H), 1.10 (3H)] and one trisubstituted olefinic proton δ 5.24 (1H, br s) attributed to H-12, which are characteristic signals of the Δ^{12}-oleanene skeleton.

The NMR spectrum of compound **1** was similar to that of 3,24-dihydroxy-22,30-epoxyolean-12-ene, and signal assignments were based on this compound.[11] In the ^{13}C NMR spectrum, **1** showed a relative downfield shift at δ 100.4 for an oxymethine carbon, compared with the C-30 oxymethylene carbon (δ 76.4) in 3,24-dihydroxy-22,30-epoxyolean-12-ene. According to the molecular formula, an OH group was likely located at C-30. Correlations of C-30 with H_3-29 (δ 0.87), H_2-21 (δ 1.60, m), and H-22 (δ 3.63, d, J = 5.7 Hz) in the HMBC spectrum fixed its position. The H-22 oxymethine displayed additional HMBC correlations with C-18 (δ 44.4), C-20 (δ 42.8), and C-28 (δ 23.9), while the H_2-24 oxymethylene signals (δ 3.26, d, J = 11.1 Hz; δ 3.82, d, J = 11.1 Hz) were correlated with C-3 (δ 79.3), C-4 (δ 43.1), and C-5 (δ 56.1).

The relative configuration of compound **1** was established by analysis of the key correlations displayed in the NOESY spectrum. NOESY correlations were observed between H-3 (δ 3.17) and H_3-23 (δ 1.07) and between H_2-24 (δ 3.26, 3.82) and H_3-25 (δ 0.87), supporting the suggested α-orientation of H-3, while the NOESY correlations between H-18 (δ 1.82) and H-12 (δ 5.24) and H-30 (δ 4.72) suggested an α-orientation of the OH at C-30. In addition, H-22 was assigned an α-orientation by the cross-peak between H-22 and H_3-28, as in compound **6**.[12,13] The structure and relative configuration of **1** was confirmed by X-ray crystallographic analysis (Supporting Information, Figure 1).

Molecules are stabilized in the crystal lattice by hydrogen bonding (Supporting Information, Figure 4). The crystal structure contains an extensive hydrogen-bond network, where all three OH groups contribute to the formation of hydrogen bonds. Apart from these hydrogen bonds, the crystal structure is held together by the stacking interactions of the almost planar hydrogen-bonded dimer molecules.

Falcatin B (**2**) was obtained as colorless needles. Its molecular formula was determined as $C_{31}H_{50}O_4$ by positive mode HRESIMS at m/z 504.4054 $[M + NH_4]^+$, which was 14 mass units more than that of **1**. The differences observed in the ^{1}H and ^{13}C NMR spectra of **2** compared with those of **1** were the occurrence of signals for H-30 and C-30 at δ_H 4.42 and δ_C 107.5 instead of at δ_H 4.72 and δ_C 100.4, respectively. In addition, the presence of a methoxy group in the structure was implied by the signals at δ_H 3.39 (3H, s) and δ_C 55.8. In the HMBC spectrum, the methoxy protons showed correlation with the carbon resonance at δ_C 107.5 (C-30). This was supported by the fragment ion at m/z 262 via a retro-Diels−Alder reaction in the EI mass spectrum. The relative configuration of compound **2** was obtained both from the similarity in coupling constants and the pattern of proton signals to those of **1** and from the NOESY spectrum. Cross-peaks between H-3 (δ 3.44) and H_3-23 (δ 1.25), H_2-24 (δ 3.34, 4.20) and H_3-25 (δ 0.89), H-22 (δ 3.80) and H_3-28 (δ 0.87), and H-18 (δ 1.87) and H-12 (δ 5.24) and H_3-30 (δ 4.42) indicated that the configuration of **2** was the same as that shown above for **1**, in relevant parts of the molecule. Finally, the structure and relative configuration of **2** were confirmed by X-ray crystallography (Supporting Information, Figure 1). As a comparison, the 3-D supramolecular network of **2** through hydrogen bonds is understandably different from that of **1**. These hydrogen bonds link the molecules into a ribbon-like structure (Supporting Information, Figure 5).

Compound **3** was also isolated as colorless needles. Its HRESIMS displayed a pseudomolecular ion peak at m/z 471.3464 $[M + H]^+$, suggesting the molecular formula $C_{30}H_{46}O_4$ and eight degrees of unsaturation. Characteristic absorption bands observed at 3332 and 1703 cm^{-1} in the IR spectrum indicated the presence of OH and ketone groups, respectively. Fragment peaks at m/z 452, 440, and 396 in the EIMS indicated the presence of OH, CH_2OH, and ketone groups. The ^{13}C NMR spectrum of **3** exhibited 30 signals (Table 1). Analysis of the ^{13}C NMR and DEPT135 spectra indicated the presence of six methyl, 10 methylene, six methine, and eight tetrasubstituted carbons. The signals at δ_C 16.0, 17.1, 19.8, 20.5, 26.3, and 28.5 in the ^{13}C NMR spectrum were attributed to six methyl carbons, while the signals at δ_C 64.4, 180.2, and 214.7 indicated the presence of an oxymethylene, a carboxyl, and a ketone in the structure, respectively. It is known that in the ^{13}C NMR spectrum of cyclic triterpenoids the signal due to an axial hydroxymethylene carbon at C-4 appears upfield (δ 63−66) to that of an equatorial hydroxymethylene carbon (δ 68−71) at C-4.[14,15] Therefore, the hydoxymethylene carbon was assigned to the axial C-24, meaning that the tertiary methyl group at δ_H 1.01 in the ^{1}H NMR spectrum was H_3-23. These data, when coupled with information from the ^{1}H NMR spectrum (six tertiary singlets at δ 0.83, 0.95, 1.01, 1.09, 1.12, and 1.13 and a pair of oxymethylene protons at δ 3.35, 3.87), were closely related to those previously reported for **8**, azukisapogenol,[9,10] but clearly different in the signals corresponding to C-2, C-3, and C-4. The H-3 and C-3 signals were absent. These observations, together with the HMBC correlations between both H_3-23 and H_2-24 and the ketone carbon at δ 214.7, were used to establish the molecular framework of **3**.

Single-crystal X-ray diffraction analysis was carried out in order to confirm the structure of **3**. The absolute configuration was determined by Flack's method with Flack's parameter determined as 0.0(3).[16] The X-ray structure (Supporting Information, Figure 2), with DMSO (crystallization solvent) in the crystal lattice, demonstrated that the chiral centers in **3** were 4*S*, 5*R*, 8*R*, 9*R*, 10*R*, 14*S*, 17*S*, 18*R*, 20*R*. Each DMSO molecule was engaged in one hydrogen bond through its oxygen atom. Similarly, the OH group of the

triterpenoid molecule was engaged in one hydrogen bond with a neighboring molecule (Supporting Information, Figure 6).

Given the absolute configuration Flack's parameters of falcatins A (**1**) (−0.3) and B (**2**) (−0.8), it was not possible to ascertain their absolute configurations about the chiral centers.[16] Taking into account the X-ray crystallographic analyses, biogenetic considerations, and chemical shift comparisons with that of **3**, the 3*S*, 4*S*, 5*R*, 8*R*, 9*R*, 10*R*, 14*S*, 17*R*, 18*S*, 20*R*, 22*R*, 30*R* configuration of falcatins A (**1**) and B (**2**) is proposed.

The known compounds (**4**−**13**) (see Supporting Information for structures of compounds **6**−**13**) were identified as melilotigenin B (**4**),[17] melilotigenin C (**5**),[17] 24-hydroxy-11-deoxoglabrolide (**6**),[12,13] olean-12-ene-3,24-diol (**7**),[8] azukisapogenol (**8**),[9,10] soyasapogenol E (**9**),[17] abrisapogenol E[18] or wistariasapogenol B[11] (**10**), soyasapogenol B (**11**),[19] 3-methyl-5-(2,2,4-trimethylcyclohexanol-3-yl)-pent-1-ene-3-ol (**12**),[20] and 3-methyl-5-(1,3,3-trimethyl-7-oxabicyclo-[2.2.1]hept-2-yl)pent-1-en-3-ol (**13**).[21,22] The structure of melilotigenin B (**4**) was confirmed by X-ray diffraction analysis (Supporting Information, Figure 3), and its packing diagram in the crystal is shown in the Supporting Information, Figure 7. Triterpenoid lactone **6** was obtained previously by the acid hydrolysis of wistariasaponin G[12] or licorice-saponin L3,[13] while **12** has been recently prepared synthetically.[20]

Compound **10** may be the first step in the dehydration cyclization to produce 3β,24-dihydroxy-22β,30-epoxyolean-12-ene, as previously hypothesized,[11] which would be oxidized to give compound **6** or falcatin A (**1**) and then the later could undergo a methylation to produce falcatin B (**2**). It is also likely that compound **10** could be oxidized first to yield an aldehyde or acid and that these compounds then spontaneously cyclize to give falcatin A (**1**) or **6**, respectively. Falcatin A (**1**) could undergo a methylation to give falcatin B (**2**) (Supporting Information, Figure 8).

In conclusion, all triterpenes isolated from *O. falcata* are of the 24-hydroxyoleanane-type and were isolated for the first time from the genus *Oxytropis*. Moreover, the occurrence of triterpenoids having a methineoxy bridge between C-22 and C-30 such as **1** and **2** is very rare in nature, as only 3β,24-dihydroxy-22β,30-epoxy-olean-12-ene has so far been obtained by acid hydrolysis of the crude saponin fraction. Accordingly, the presence of these compounds (**1**−**11**) in the genus *Oxytropis* is of considerable chemotaxonomic interest. Sesquiterpene **12** was isolated as a new natural product, while **13** has been reported only from the genus *Artemisia* (Compositae family).[21]

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer model 341 polarimeter with a 1 dm cell. Melting points were determined on an X-4 Digital Display micro-melting point apparatus, uncorrected. UV spectra were measured on a Shimadzu UV-260 spectrophotometer. IR spectra were obtained on a Nicolet NEXUS 670 FT-IR spectrometer. NMR spectra were recorded on Varian INOVA-300 and Varian INOVA-400 spectrometers. Chemical shifts are given on a δ (ppm) scale using TMS as internal standard. EIMS and HRESIMS were carried out on a VG ZABHS mass spectrometer and a Bruker APEX II mass spectrometer, respectively. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer, and the structure was solved by direct methods using Bruker SHELXS-97. Silica gel (200−300 mesh) used for column chromatography and silica GF_{254} (10−40 μm) for TLC were both supplied by the Qingdao Marine Chemical Factory, Qingdao, People's Republic of China. TLC was detected at 254 nm, and spots were visualized by spraying with 5% H_2SO_4 in C_2H_5OH (v/v) followed by heating.

Plant Material. *Oxytropis falcata* was collected from Sunan County, Gansu Province, People's Republic of China, in June 2006, and identified by adjunct Prof. Huan-Yang Qi. A voucher specimen (No. ZY-0601) has been deposited in our laboratory.

Extraction and Isolation. Plant material (aerial parts 3.5 kg, roots 0.5 kg) was air-dried, ground, and exhaustively extracted with 95% EtOH at room temperature. The EtOH extract of each part of the plant was suspended in water and then partitioned successively with petroleum ether, EtOAc, and *n*-BuOH. The EtOAc-soluble fractions (aerial parts 113 g, roots 12 g) were processed separately. The EtOAc-soluble fraction (100 g) of the aerial parts of *O. falcata* was subjected to silica gel CC, using a step gradient-elution technique, employing mixtures of CH_2Cl_2−EtOAc and MeOH as solvents, to afford five fractions (F1, CH_2Cl_2, 23 g; F2, 10% CH_2Cl_2−EtOAc, 18 g; F3 25% CH_2Cl_2−EtOAc, 15 g; F4, 50% CH_2Cl_2−EtOAc 16 g; F5, MeOH, 20 g) according to TLC analysis. Fraction F3 was chromatographed on silica gel with a petroleum ether−EtOAc gradient system to give five subfractions. Repeated chromatography of subfraction 3 over silica gel (petroleum ether−EtOAc, 8:1; petroleum ether−acetone 3:1) followed by recrystallization yielded **5** (2.6 mg), **7** (3.1 mg), and **13** (10.2 mg). Further purification of subfraction 5 through repeated chromatography with CH_2Cl_2−EtOAc (7:1) as eluent yielded **6** (30.8 mg), **4** (2.0 mg), **3** (4.3 mg), **12** (7.2 mg), and **9** (13.7 mg), respectively. Fraction F4 was separated using the same procedure as F3 to afford **2** (4.2 mg), **1** (9.0 mg), **10** (6.5 mg), and **8** (8.5 mg), respectively. Likewise, a similar isolation procedure adopted for the EtOAc-soluble fraction (10 g) of the roots of *O. falcata* afforded **5** (7.3 mg), **6** (1.8 mg), **8** (11.1 mg), and **11** (15.0 mg).

Falcatin A (1): colorless needles (MeOH); mp 273−274 °C; $[\alpha]^{20}_D$ +45 (*c* 0.11, MeOH); IR (neat) ν_{max} 3376, 2923, 1652, 1458, 1118, 1090, 1045 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 5.80 (1H, d, J = 6.0 Hz, OH-30), 5.24 (1H, br s, H-12), 4.95 (1H, d, J = 4.8 Hz, OH-3), 4.72 (1H, d, J = 6.3 Hz, H-30), 4.07 (1H, d, J = 5.4 Hz, HO-24), 3.82 and 3.26 (2H, ABq, J = 11.1 Hz, H-24), 3.63 (1H, d, J = 5.7 Hz, H-22), 3.17 (1H, m, H-3), 1.82 (1H, m, H-18), 1.60 (2H, m, H-21), 1.10 (3H, s, H-27), 1.07 (3H, s, H-23), 0.87 (3 × 3H, s, H-25, H-26, H-30), 0.76 (3H, s, H-28); ^{13}C NMR (DMSO-d_6, 75 MHz) data see Table 1; EIMS *m*/*z* 472 (1%), 454 (4%), 436 (1%), 426 (2%), 248 (92%), 230 (100%), 224 (16%); HRESIMS *m*/*z* 459.3446 (calcd for $C_{30}H_{48}O_4$+Na, 459.3445).

X-ray Crystallography of 1. A colorless crystal was obtained from a solution of DMSO, triclinic space group $P1$, a = 6.9430(8) Å, b = 7.2493(8) Å, c = 15.2539(17) Å, V = 664.71(13) Å^3, Z = 1, R = 0.013 ($F^2 > 2\sigma$), R_w = 0.0861 (all F^2) for 2835 unique data having 2θ < 51.1° and 326 refined parameters.

Falcatin B (2): colorless needles ($CDCl_3$); mp 281−283 °C; $[\alpha]^{20}_D$ +40 (*c* 0.13, MeOH); IR (neat) ν_{max} 3357, 2921, 1653, 1450, 1120, 1043, 1018 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.24 (1H, br s, H-12), 4.42 (1H, br s, H-30), 4.20 and 3.34 (2H, ABq, J = 10.8 Hz, H-24), 3.80 (1H, d, J = 4.0 Hz, H-22), 3.44 (1H, dd, J = 2.4, 11.7 Hz, H-3), 3.39 (3H, s, CH_3-30), 1.87 (1H, m, H-18), 1.25 (3H, s, H-23), 1.13 (3H, s, H-27), 0.96 (3H, s, H-30), 0.91 (3H, s, H-26), 0.89 (3H, s, H-25), 0.87 (3H, s, H-28); ^{13}C NMR ($CDCl_3$, 100 MHz) data see Table 1; EIMS *m*/*z* 486 (1%), 455 (3%), 454 (7%), 426 (2%), 262 (81%), 230 (74%), 224 (23%), 202 (100%); HRESIMS *m*/*z* 504.4054 (calcd for $C_{31}H_{50}O_4$+NH_4, 504.4047).

X-ray Crystallography of 2. A colorless crystal was obtained from a solution of $CHCl_3$−CH_3COCH_3 (1:2), monoclinic space group $C2$, a = 12.3341(10) Å, b = 7.3877(10) Å, c = 30.799(3) Å, V = 2781.8(5) Å^3, Z = 4, R = 0.015 ($F^2 > 2\sigma$), R_w = 0.0950 (all F^2) for 4759 unique data having 2θ < 51.1° and 326 refined parameters.

3-Oxo-azukisapogenol (3): colorless needles (MeOH); mp 262−264 °C; $[\alpha]^{20}_D$ +20 (*c* 0.11, MeOH); IR (neat) ν_{max} 3332, 2925, 1703, 1458, 1379 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 5.21 (1H, br s, H-12), 3.86 and 3.35 (2H, ABq, J = 11.1 Hz, H-24), 2.70 (1H, m, H-18), 1.13 (3H, s, H-25), 1.12 (3H, s, H-30), 1.09 (3H, s, H-27), 1.01 (3H, s, H-23), 0.95 (3H, s, H-26), 0.83 (3H, s, H-28); ^{13}C NMR (DMSO-d_6, 75 MHz) data see Table 1; EIMS *m*/*z* 470 (0.5%), 452 (0.1%), 440 (2%), 425 (1%), 396 (6%), 379 (3%), 248 (97%), 222 (3%), 203 (14%), 187 (96%), 173 (100%); HRESIMS *m*/*z* 471.3464 (calcd for $C_{30}H_{46}O_4$+H, 471.3469).

X-ray Crystallography of 3. A colorless crystal was obtained from a solution of DMSO, orthorhombic space group $P2_12_12_1$, a = 7.2899(4) Å, b = 11.7817(6) Å, c = 36.3289(17) Å, V = 3120.2(3) Å^3, Z = 4, R = 0.049 ($F^2 > 2\sigma$), R_w = 0.1809 (all F^2) for 2847 unique data having 2θ < 39.8° and 356 refined parameters.

X-ray Crystallography of 4. A colorless crystal was obtained from a solution of $CHCl_3$−CH_3COCH_3 (1:2), monoclinic space group $P2_1$, a = 12.3700(9) Å, b = 7.2582(5) Å, c = 29.428(2) Å, V = 2613.8(3) Å^3, Z = 2, R = 0.0279 ($F^2 > 2\sigma$), R_w = 0.1063 (all F^2) for 6154 unique data having 2θ < 44.76° and 611 refined parameters.

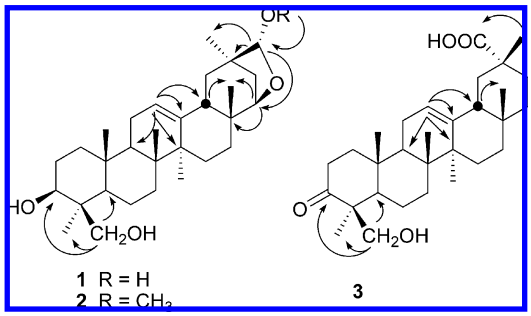


Figure 1. Selected HMBC correlations for **1**−**3**.

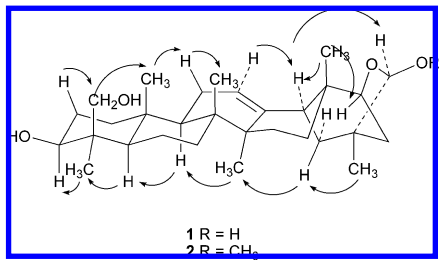


Figure 2. Selected NOESY correlations for **1** and **2**.

Crystallographic Data of 1−4. Crystallographic data for the structures of falcatins A (**1**) and B (**2**), 3-oxo-azukisapogenol (**3**), and melilotigenin B (**4**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 709718−709721. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. This paper is dedicated to the 100th anniversary of Lanzhou University. We are grateful to Dr. X.-L. Tang (College of Chemistry and Chemical Engineering, Lanzhou University) for his valuable technical assistance. This work was financially supported by the Foundation for the National Natural Science Foundation of China (No. NSFC 20621091), the National 863 Program of China (No. 2007AA09Z403), and National Key Technology Research and Development Program of China (No. 2007BAI37B05).

Supporting Information Available: Structures of compounds **6**−**13**, network of hydrogen bonds of compounds **1**−**4**, NMR spectra (^{1}H, ^{13}C NMR, gHMBC, and NOESY of **1**, **2**; ^{1}H, ^{13}C NMR, and gHMBC of **3**) of compounds **1**−**3**, plausible biogenetic pathways to compounds **1**, **2**, and **6**, and CIF files of compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) James, L. F.; Panter, K. E.; Gaffield, W.; Molyneux, R. J. *J. Agric. Food Chem.* **2004**, *52*, 3211–3230.
(2) Lei, J. F.; Zhang, Y. S.; Chen, L. J.; Liu, H. L.; He, G. J. *Faming Zhuanli Shenqing Gongkai Shuomingshu* CN 101181372, 2008.
(3) Chen, W. H.; Ren, Z. Y.; Wang, R.; Shi, Y. P. *Anal. Sci.: X-ray Struct. Anal. Online* **2008**, *24*, x209–x211.
(4) Marii, T.; Hiroyuki, F.; Setsuko, S.; Motoyoshi, S.; Fumiyuki, K. *Chem. Pharm. Bull.* **2006**, *54*, 915–917.
(5) Rao, K. V. *Tetrahedron* **1964**, *20*, 973–977.
(6) Biemann, K. *Mass Spectrometry: Organic Chemical Applications*; McGraw-Hill: New York, 1962; p 347.
(7) Budziciewicz, H.; Djerassi, C.; Williams, D. H. *Structure Elucidation of Natural Products by Mass Spectrometry, Vol.* Π; Holden Day: San Franciso, 1964.
(8) Tanaka, R.; Tabuse, M.; Matsunaga, S. *Phytochemistry* **1988**, *27*, 3563–3567.
(9) Yao, S. Y.; Ma, Y. B.; Tang, Y.; Chen, J. J.; Zhang, X. M. *Zhong Guo Zhong Yao Za Zhi* **2007**, *32*, 1660–1662.
(10) Kitagawa, I.; Wang, H. K.; Saito, M.; Yoshikawa, M. *Chem. Pharm. Bull.* **1983**, *31*, 664–673.
(11) Konoshima, T.; Kozuka, M.; Haruna, M.; Ito, K.; Kimura, T. *Chem. Pharm. Bull.* **1989**, *37*, 1550–1553.
(12) Konoshima, T.; Kozuka, M.; Haruna, M.; Ito, K. *J. Nat. Prod.* **1991**, *54*, 830–836.
(13) Kitagawa, I.; Hori, K.; Uchida, E.; Chen, W. Z.; Yoshikawa, M.; Ren, J. L. *Chem. Pharm. Bull.* **1993**, *41*, 1567–1572.
(14) Agrawal, P. K.; Jain, D. C. *Prog. NMR Spectrosc.* **1992**, *24*, 1–90.
(15) Mahato, S. B.; Kundu, A. P. *Phytochemistry* **1994**, *37*, 1517–1575.
(16) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.
(17) Macias, F. A.; Simonet, A. M.; Galindo, J. C. G.; Pacheco, P. C.; Sanchez, J. A. *Phytochemistry* **1998**, *49*, 709–717.
(18) Takeshita, T.; Hamada, S.; Nohara, T. *Chem. Pharm. Bull.* **1989**, *37*, 846–848.
(19) Baxter, R. L.; Price, K. R.; Fenwick, G. R. *J. Nat. Prod.* **1990**, *53*, 298–302.
(20) Justicia, J.; Rosales, A.; Buñuel, E.; Oller-Lŏpez, J. L.; Valdivia, M.; Haïdour, A.; Oltra, J. E.; Barrero, A. F.; Cárdenas, D. J.; Cuerva, J. M. *Chem.—Eur. J.* **2004**, *10*, 1778–1788.
(21) Marco, L. A.; Sanz, J. F.; Yuste, A.; Carda, M.; Jakupovic, J. *Phytochemistry* **1991**, *30*, 3661–3668.
(22) Barrero, A. F.; Alvarez-Manzaneda, E. J.; Chahboun, R.; Rivas, A. R.; Palomino, P. L. *Tetrahedron* **2000**, *56*, 6099–6113.

NP900199X