# Chemical Constituents from *Pedicularis rex* C. B. Clarke

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One new ionone glycoside, pedicurexoside (**1**), one new flavonoid, 5, 4′-dihydroxy-3′-methoxy-flavone-7-*O*-6″-*n*-butyryl-$\beta$-D-glucopyranoside (**2**), two new iridoid glycosides, 6-*O*-ethyl-aucubin (**7**), 6-*O*-ethyl-epiaucubin (**8**), and one new phenylpropanoid glycoside, 4-hydroxy-phenylpropenyl-$\alpha$-L-rhamnopyranosyl-(1 → 3)-4-*O*- feruloyl-$\beta$-D-glucopyranoside (**13**), together with eleven known compounds, apigenin (**3**), luteolin (**4**), chrysoeriol (**5**), luteolin-7-*O*-$\beta$-D-glucopyranoside (**6**), aucubin (**9**), yuheinoside (**10**), euphroside (**11**), mussaenoside (**12**), verbascoside (**14**), martynoside (**15**) and isomartynoside (**16**), were isolated from *Pedicularis rex*. The structures of **1** – **16** were elucidated mainly by 1D and 2D NMR techniques, MS evidence and chemical methods. The ionone derivative with thirteen carbon atoms was found in *Pedicularis* plants for the first time.

*Key words:* Scrophulariaceae, *Pedicularis rex*, Pedicurexoside, Flavonoid, Iridoid

## Introduction

*Pedicularis* L. is widely distributed in the world, comprising about 300 species in China [1]. Some species of this genus are used to treat diseases [2]. Up to now, many types of compounds have been isolated from *Pedicularis* species, such as iridoids, phenylpropanoids and flavonoids *etc*. [3]. *Pedicularis rex* C. B. Clarke (Scrophulariaceae) is used as a folk medicine for the treatment of measles, chronic hepatitis and rheumatism paralysis [4]. However, there has been no report on its chemical constituents. In this paper, we report the structure elucidation of five new compounds, **1**, **2**, **7**, **8** and **13**, from this plant (Fig. 1).

## Results and Discussion

Compound **1** was obtained as a white amorphous powder. The FAB$^-$-MS spectrum gave a quasi-molecular ion peak at *m/z* = 385 [M–1]$^-$ and the HR-TOF-MS suggested a molecular formula of $C_{19}H_{30}O_8$ (*m/z* = 385.1866, calcd. 385.1862, [M–1]$^-$). The IR spectrum (KBr) showed characteristic absorption bands at 3418, 1651 and 1606 cm$^{-1}$ assignable to hydroxyl and $\alpha$, $\beta$-unsaturated carbonyl groups. The $^1$H and $^{13}$C NMR spectra (see Table 1) of **1** revealed the presence of three methyls [$\delta$ = 1.14, 1.82, 2.31 (all s, H-12, 13, 10)], three methylenes [$\delta$ = 1.29 (t, *J* = 12.1 Hz), 2.24 (m), H-2; 2.06 (dd, *J* = 17.4, 9.5 Hz), 2.43 (dd, *J* = 17.5, 5.3 Hz), H-4; 3.43 (d, *J* = 9.7 Hz), 3.79 (d, *J* = 9.7 Hz), H-11], one methine bearing an oxygen function [$\delta$ = 4.10 (m), H-3], and one *trans*-olefin [$\delta$ = 6.14, 7.34 (both d, *J* = 16.4 Hz, H-8, 7)], together with a $\beta$-glucopyranosyl group [$\delta$ = 4.22 (d, *J* = 7.8 Hz, H-1′)]. The acid hydrolysis of **1** with 5 % aqueous HCl liberated D-glucose. The aglycon **1a** was obtained by enzymatic hydrolysis of **1** with cellulase. The structure of **1** was confirmed by $^1$H, $^1$H COSY and HMBC experiments.

The $^1$H, $^1$H COSY experiment on **1** indicated the presence of the partial structures written in bold lines, and in the HMBC experiment long-range correlations were observed between the following protons and carbons: H-2, H-11, H-12 and C-1; H-11 and C-2; H-2, H-4 and C-3; H-4, H-13 and C-5; H-7, H-12, H-13 and C-6; H-7, H-8, H-10 and C-9; H-1′ and C-11 (Fig. 2). Comparison of the $^{13}$C NMR spectra of **1** with **1a** shows that the signal of C-1 was shifted upfield by 2.5 ppm, and the one of C-11 downfield by 7.2 ppm, which further indicated that $\beta$-D-glucose linked at C-11. The relative configuration of **1** was determined by a ROESY experiment, in which correlations were observed between H-3 and H-11 (Fig. 2), suggesting that H-3 and H-11 are in the same orientation. The negative optical rotations of **1** and **1a** [$[\alpha]_D^{29} = -69.5^\circ$ (*c* =

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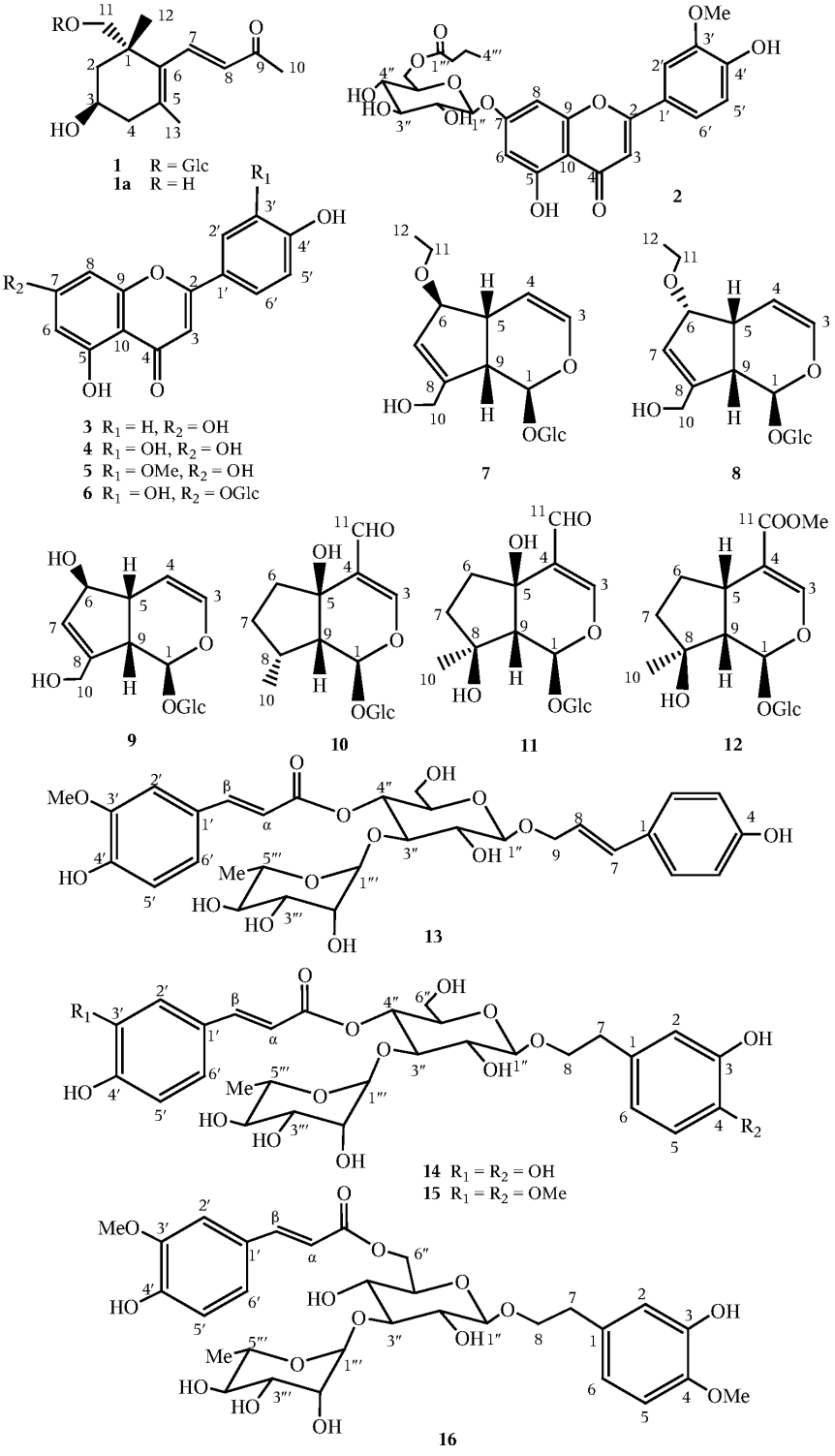


Fig. 1. Compounds **1** – **16**.

Table 1. $^{1}$H (400 MHz) and $^{13}$C NMR (100 MHz) data of **1** and **1a** (in $CD_3OD$; *J* values in Hz in parentheses).

| | **1** | | **1a** | |
|---|---|---|---|---|
| No. | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ |
| 1 | 42.3(s) | | 44.8(s) | |
| 2 | 43.8(t) | 1.29(t, 1H, 12.1) | 43.5(t) | 1.27(t, 1H, 12.0) |
| | | 2.24(m, 1H) | | 2.27(m, 1H) |
| 3 | 64.5(d) | 4.10(m, 1H) | 64.5(d) | 4.05(m, 1H) |
| 4 | 43.1(t) | 2.06(dd, 1H, 17.4, 9.5) | 43.2(t) | 2.06(dd, 1H, 17.9, 8.7) |
| | | 2.43(dd, 1H, 17.5, 5.3) | | 2.42(dd, 1H, 17.4, 5.3) |
| 5 | 136.8(s) | | 136.7(s) | |
| 6 | 133.6(s) | | 133.7(s) | |
| 7 | 144.9(d) | 7.34(d, 1H, 16.4) | 144.8(d) | 7.30(d, 1H, 16.4) |
| 8 | 133.6(d) | 6.14(d, 1H, 16.4) | 133.6(d) | 6.11(d, 1H, 16.4) |
| 9 | 201.5(s) | | 201.2(s) | |
| 10 | 27.2(q) | 2.31(s, 3H) | 27.2(q) | 2.29(s, 3H) |
| 11 | 76.8(t) | 3.43(d, 1H, 9.7) | 69.6(t) | 3.36(d, 1H, 11.0) |
| | | 3.79(d, 1H, 9.7) | | 3.45(d, 1H, 11.1) |
| 12 | 25.7(q) | 1.14(s, 3H) | 25.3(q) | 1.07(s, 3H) |
| 13 | 22.1(q) | 1.82(s, 3H) | 22.1(q) | 1.81(s, 3H) |
| Glucose | | | | |
| 1′ | 104.6(d) | 4.22(d, 1H, 7.8) | | |
| 2′ | 75.1(d) | 3.19(m, 1H) | | |
| 3′ | 78.1(d) | 3.34(m, 1H) | | |
| 4′ | 71.5(d) | 3.28(m, 1H) | | |
| 5′ | 77.8(d) | 3.26(m, 1H) | | |
| 6′ | 62.6(t) | 3.67(dd, 1H, 11.9, 5.3) | | |
| | | 3.87(dd, 1H, 12.1, 1.8) | | |

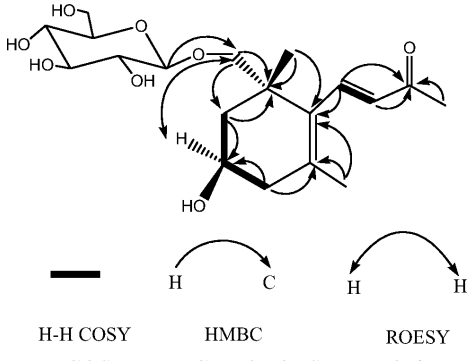


Fig. 2. H-H COSY, HMBC, and ROESY correlations of **1**.

0.61, $CH_3OH$); $[\alpha]_D^{21} = -125.7°$ ($c$ = 0.35, $CH_3OH$)] agree with the related compounds icariside $B_4$ and deglycosyl icariside $B_4$ [$[\alpha]_D^{25} = -79.1°$ ($c$ = 0.79, $CH_3OH$); $[\alpha]_D^{25} = -102°$ ($c$ = 0.95, $CHCl_3$)] reported in the literature [5, 6]. So the structure of compound **1** was determined as 3$\beta$-hydroxy-$\beta$-ionone 11$\alpha$-*O*-$\beta$-D-glucopyranoside, which was named pedicurexoside.

Compound **2** was obtained as a yellow powder. The FAB$^-$-MS spectrum had a quasi-molecular ion peak at *m/z* = 531 $[M-1]^-$, and the HR-TOF-MS allowed the molecular formula of $C_{26}H_{28}O_{12}$ to be determined (*m/z* = 531.1504, calcd. 531.1502, $[M-1]^-$). The compound exhibited IR absorption bands at 3425 and 1630 cm$^{-1}$ and UV maximum absorptions (206, 269 and 342 nm), which were characteristic of a flavonoid. The $^{1}$H and $^{13}$C NMR spectral data (see

Table 2. $^{1}$H (500 MHz) and $^{13}$C NMR (100 MHz) data of **2** (in DMSO; *J* values in Hz in parentheses).

| No | $\delta_C$ | $\delta_H$ | HMBC |
|---|---|---|---|
| 2 | 162.4(s) | | H-3, H-2′, H-6′, H-5′ |
| 3 | 103.5(d) | 6.97(1H, s) | |
| 4 | 182.0(s) | | H-3 |
| 5 | 164.3(s) | | |
| 6 | 99.4(d) | 6.46(1H, d, 1.9) | H-8, 5-OH |
| 7 | 161.2(s) | | H-6, H-8, H-1″, 5-OH |
| 8 | 94.9(d) | 6.86(1H, d, 2.0) | H-6 |
| 9 | 156.9(s) | | H-8 |
| 10 | 105.5(s) | | H-3, H-6, H-8, 5-OH |
| 1′ | 121.3(s) | | H-3 |
| 2′ | 110.5(d) | 7.57(1H, s) | H-6′ |
| 3′ | 148.1(s) | | H-2′, H-5′, 3′-OMe |
| 4′ | 151.0(s) | | H-2′, H-5′ |
| 5′ | 115.8(d) | 6.94(1H, d, 8.8) | |
| 6′ | 120.5(d) | 7.58(1H, overlapped) | H-3, H-2′, H-5′ |
| 3′-OMe | 56.0(q) | 3.88(3H, s) | |
| 1″ | 99.4(d) | 5.29(1H, d, 7.2) | H-2″, H-3″ |
| 2″ | 72.8(d) | 3.30(1H, m) | |
| 3″ | 75.2(d) | 4.16(1H, m) | H-2″ |
| 4″ | 71.2(d) | 3.41(1H, m) | H-3″ |
| 5″ | 75.5(d) | 3.34(1H, m) | |
| 6″ | 64.4(t) | 4.07(2H, m) | H-2″, H-3″ |
| 1‴ | 168.6(s) | | H-6″ |
| 2‴ | 30.0(t) | 1.53(2H, m) | H-6″ |
| 3‴ | 18.4(t) | 1.29(2H, m) | H-6″, H-1″, H-2″ |
| 4‴ | 13.4(q) | 0.81(3H, t, 7.4) | H-2″, H-3″ |

Table 3. $^1$H (400 MHz) and $^{13}$C NMR (100 MHz) data of **7**, **8** and **9** (in $CD_3OD$; *J* values in Hz in parentheses).

| | **7** | | **8** | | **9** | |
|---|---|---|---|---|---|---|
| No. | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ |
| 1 | 97.3(d) | 4.99(overlapped) | 98.2(d) | 5.06(d, 1H, 7.1) | 97.7(d) | 4.98(d, 1H, 7.1) |
| 3 | 141.6(d) | 6.28(dd, 1H, 6.1, 1.8) | 142.7(d) | 6.38(dd, 1H, 6.2, 1.7) | 141.6(d) | 6.33(dd, 1H, 6.1, 1.8) |
| 4 | 105.9(d) | 5.01(overlapped) | 102.6(d) | 4.91(dd, 1H, 6.1, 3.9) | 105.7(d) | 5.12(dd, 1H, 6.1, 3.9) |
| 5 | 43.2(d) | 2.76(m, 1H) | 40.9(d) | 2.91(m, 1H) | 46.2(d) | 2.68(m, 1H) |
| 6 | 90.6(d) | 4.21(m, 1H) | 84.9(d) | 4.38(overlapped) | 82.8(d) | 4.46(m, 1H) |
| 7 | 127.5(d) | 5.85(d, 1H, 1.4) | 128.2(d) | 5.91(s, 1H) | 130.3(d) | 5.79(*br s*, 1H) |
| 8 | 149.2(s) | | 150.5(s) | | 148.0(s) | |
| 9 | 47.9(d) | 2.90(t, 1H, 6.9) | 47.7(d) | 2.63(t, 1H, 7.0) | 47.9(d) | 2.92(t, 1H, 7.3) |
| 10 | 61.3(t) | 4.16(d, 1H, 15.9) | 61.5(t) | 4.18(d, 1H, 11.8) | 61.4(t) | 4.19(d, 1H, 15.4) |
| | | 4.34(d, 1H, 15.9) | | 4.39 (overlapped) | | 4.37(d, 1H, 15.3) |
| 11 | 65.8(t) | 3.59(m, 2H) | 66.0(t) | 3.53(m, 1H) | | |
| | | | | 3.60(overlapped) | | |
| 12 | 15.8(q) | 1.19(t, 3H, 7.1) | 15.7(q) | 1.14(t, 3H, 7.0) | | |
| Glucose | | | | | | |
| 1′ | 99.8(d) | 4.66(d, 1H, 7.9) | 100.0(d) | 4.67(d, 1H, 7.9) | 99.9(d) | 4.70(d, 1H, 7.9) |
| 2′ | 74.9(d) | 3.21(m, 1H) | 75.0(d) | 3.21(m, 1H) | 74.9(d) | 3.24(t, 1H, 8.1) |
| 3′ | 78.3(d) | 3.28(m, 1H) | 78.2(d) | 3.27(m, 1H) | 78.2(d) | 3.29(m, 1H) |
| 4′ | 71.6(d) | 3.30(m, 1H) | 71.6(d) | 3.30(m, 1H) | 71.5(d) | 3.39(m, 1H) |
| 5′ | 77.9(d) | 3.27(m, 1H) | 77.9(d) | 3.38(m, 1H) | 77.9(d) | 3.34(m, 1H) |
| 6′ | 62.7(t) | 3.63(overlapped) | 62.7(t) | 3.66(overlapped) | 62.6(t) | 3.67(dd, 1H, 12.0, 5.3) |
| | | 3.85(d, 1H, 11.9) | | 3.83(d, 1H, 11.5) | | 3.88(d, 1H, 11.6) |

Table 2) for **2** revealed the presence of two methyls, three methylenes, 11 methines and 10 quaternary carbon atoms, in which signals of a D-glucose, a methoxy and a butyryl group were observed. The anomeric proton of the glucose at $\delta$ = 5.29 (1H, d, *J* = 7.2 Hz) suggested that the glucose was in $\beta$-orientation. The $^1$H NMR spectra showed typical signals [$\delta_H$ = 6.97 (1H, s, H-3), 6.46 (1H, d, *J* = 1.9 Hz, H-6), 6.86 (1H, d, *J* = 2.0 Hz, H-8), 7.57 (1H, s, H-2′), 6.94 (1H, d, *J* = 8.8 Hz, H-5′), 7.58 (1H, overlapped)] of a luteolin-like flavone skeleton [7]. In the HMBC spectrum (see Table 2), the correlations between $\delta_H$ = 5.29 (1H, d, *J* = 7.2 Hz, H-1″ of Glc) and $\delta_C$ = 161.2 (C-7) suggested that the $\beta$-D-glucose is linked at C-7, and the correlations between $\delta_H$ = 3.88 (3H, s, -OMe) and $\delta_C$ = 148.1 (C-3′), and $\delta_H$ = 4.07 (2H, m, H-6″) and $\delta_C$ = 168.6 (C-1‴) indicated that methoxy and butyryl groups are linked at C-3′ and C-6″, respectively. From the above results, compound **2** was determined to be 5, 4′-dihydroxy-3′-methoxyflavone-7-*O*-6″-*n*-butyryl-$\beta$-D-glucopyranoside.

Compounds **7** and **8** were obtained as white amorphous powders. The FAB$^-$-MS spectrum gave the same quasi-molecular ion peak at *m/z* = 373 [M–1]$^-$ and the HR-TOF-MS provided the same molecular formula of $C_{17}H_{26}O_9$ (*m/z* = 373.1490 and 373.1500, calcd. 373.1498, [M–1]$^-$). The IR spectrum (KBr) of compounds **7** and **8** showed characteristic absorption bands due to hydroxyls (3429; 3425 cm$^{-1}$), double bonds (1644; 1642 cm$^{-1}$), and ether functions (1077, 1044, 1014; 1079, 1049, 1018 cm$^{-1}$). It was evident from the $^1$H and $^{13}$C NMR spectra (see Table 3) that both **7** and **8** contained an ethyl moiety, and that both were very similar to aucubin. Comparing the $^{13}$C NMR spectrum of **7** with that of aucubin (**9**) (see Table 3), C-6 showed a significant downfield shift (+7.8 ppm), suggesting that the position of the ethyl group was at C-6, and the HMBC correlation of $\delta_H$ = 3.59 (2H, m, H-11) to $\delta_C$ = 90.6 (C-6) confirmed the above results. Moreover, the difference between compound **8** and 6-epiaucubin [8] (downfield shift +8.8 ppm, C-6) was identical with that of compound **7** and aucubin, indicating that the ethyl group is linked to C-6. In the HMBC spectrum of **8**, the correlation between $\delta_H$ = 3.53 (1H, m, H-11), 3.60 (1H, overlapped, H-11) and $\delta_C$ = 84.9 (C-6) proved the ethyl group in **8** to be also linked to C-6. Thus, compound **7** was determined to be 6-*O*-ethyl-aucubin and **8** to be 6-*O*-ethyl-epiaucubin.

Compound **13** was obtained as a white amorphous powder. The FAB$^-$-MS spectrum gave a quasi-molecular ion peak at *m/z* = 633 [M–1]$^-$ and the HR-TOF-MS provided a molecular formula of $C_{31}H_{38}O_{14}$ (*m/z* = 633.2197, calcd. 633.2183, [M–1]$^-$). The $^1$H and $^{13}$C NMR spectra of **13** revealed the presence of two methyls, two methylenes, 21 methines and six quaternary carbon atoms and indicated that **13** was a phen-

ylpropenyl diglycoside (glucose and rhamnose) with a feruloyl group. The $^1$H and $^{13}$C NMR signals of the acyl moiety of **13** were similar to those of martynoside [9]. In the NMR spectra, the signal of a 4-hydroxyphenylpropenyl group was observed. In the HMBC spectrum, long-range correlations were observed between the following protons and carbons: $\delta_H$ = 4.44 (1H, $J$ = 7.9 Hz, H-1″ of Glc) and $\delta_C$ = 71.3 (C-9), $\delta_H$ = 4.87 (1H, m, H-4″ of Glc) and $\delta_C$ = 168.4 (C=O), and $\delta_H$ = 5.19 (1H, d, $J$ = 1.4 Hz, H-1‴ of Rha) and $\delta_C$ = 81.6 (C-3″ of Glc), indicating that phenylpropenyl, feruloyl, and rhamonosyl groups are linked with C-1″, C-4″, C-3″ of the glucose, respectively. On the basis of the above analysis, **13** was identified as 4-hydroxy-phenylpropenyl-$\alpha$-L-rhamnopyranosyl-(1 → 3)-4-*O*-feruloyl-$\beta$-D-glucopyranoside.

By MS, $^1$H and $^{13}$C NMR data, eleven known compounds were determined to be present: apigenin (**3**) [10], luteolin (**4**) [7], chrysoeriol (**5**) [11], luteolin-7-*O*-$\beta$-D-glucopyranoside (**6**) [12], aucubin (**9**) [13], yuheinoside (**10**) [14], euphroside (**11**) [15], mussaenoside (**12**) [16], verbascoside (**14**) [17], martynoside (**15**) [9], and isomartynoside (**16**) [18].

## Experimental Section

*General*

Optical rotations were measured with a Horbia SEAP-300 polarimeter. IR spectra were obtained on a Bio-Rad FTS-135 spectrophotometer with KBr pellets. UV spectra were taken on a Shimadzu 2401PC spectrophotometer. FAB-MS and HR-TOF-MS were recorded on a VG Auto Spec-3000 spectrometer. 1D- and 2D-NMR spectra were recorded on Bruker AM-400 and DRX-500 spectrometers with TMS as internal standard. Column chromatography was performed over silica gel (200 – 300 mesh, Qingdao Marine Chemical Inc., China) and Sephedex LH-20 (25 – 100 $\mu$m, Pharmacia Fine Chemical Co., Ltd., Sweden), respectively.

*Plant material*

The plant material was collected in Zhong Dian, Yunnan Province of China in August 2004 and identified by Prof. Wang Hong, Kunming Institute of Botany, Chinese Academy of Sciences. The voucher specimen (KUN 0473556) was deposited in the herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

*Extraction and isolation*

Dried whole plant material (11 kg) of *P. rex* was extracted with 95 % ethanol three times (each for one week) at r. t. After concentration of the combined extracts under reduced pressure, the residue was dissolved in hot water and extracted successively with petroleum ether and *n*-BuOH. The *n*-BuOH portion was divided into 5 fractions (Frs. 1 – 5) over a silica gel column eluted with $CHCl_3$/MeOH (30 : 1) followed by increasing concentrations of MeOH. Fr. 2 was separated further by CC on silica gel and Sephadex LH-20 to give compounds **3** (100 mg), **4** (40 mg) and **5** (50 mg). Fr. 3 was purified by repeated CC and Sephadex LH-20 to obtain **1** (80 mg), **9** (31 mg), **10** (13 mg), **11** (9 mg), **12** (38 mg), **13** (6 mg), **14** (300 mg), and two mixture fractions (Fr. A and B). Fr. A was then purified by HPLC (Zorbax ODS-C18, MeOH/$H_2O$, 1 : 4) to afford compounds **7** (8 mg) and **8** (9 mg). Compounds **15** (500 mg) and **16** (10 mg) were obtained from Fr. B by HPLC (Zorbax ODS-C18, MeOH/$H_2O$, 2 : 3). Fr. 5 was subjected to chromatography over Sephadex LH-20 to give compounds **2** (6 mg) and **6** (14 mg).

*Acid hydrolysis of **1***

A solution of **1** (5 mg) in 5 % aqueous HCl was heated under reflux for 6 h. After cooling, the reaction mixture was neutralized with an aqueous $NaHCO_3$ solution. Then, the solution was extracted with EtOAc. The aqueous layer was subjected to TLC analysis. Identification of D-glucose present in the aqueous layer was carried out by comparison of its $R_f$ shift with that of an authentic sample.

*Enzymatic hydrolysis of **1** with cellulase*

A solution of **1** (12 mg) in $H_2O$ (2 mL) was treated with cellulase (12 mg) and the solution was stirred at r. t. for 12 h. Then, the solution was extracted with EtOAc. The EtOAc portion was subjected to chromatography over silica gel to obtain **1a** (7 mg).

*Pedicurexoside (**1**):* white amorphous powder. – $[\alpha]_D^{29}$ = −69.5° ($c$ = 0.61, $CH_3OH$). – UV (MeOH): $\lambda(\log\varepsilon)$ = 203 (3.81), 291 (3.77), 364 (1.97) nm. – IR (KBr): $\nu$ = 3418, 2920, 2877, 1651, 1606, 1368, 1079, 1040 cm$^{-1}$. – $^1$H NMR (400 MHz, $CD_3OD$) and $^{13}$C NMR (100 MHz, $CD_3OD$) data are shown in Table 1. – FAB$^-$-MS: *m/z* (%) = 385 (100) [M–1]$^-$. – HR-TOF-MS: *m/z* = 385.1866 (calcd. 385.1862 for $C_{19}H_{29}O_8$, [M–1]$^-$).

*Aglycon (**1a**):* white amorphous powder. – $[\alpha]_D^{21}$ = −125.7° ($c$ = 0.35, $CH_3OH$). – $^1$H NMR (400 MHz, $CD_3OD$) and $^{13}$C NMR (100 MHz, $CD_3OD$) data are shown in Table 1. – FAB$^+$-MS: *m/z* (%) = 225 (100) [M+1]$^+$.

*5,4′-Dihydroxy-3′-methoxyflavone-7-O-6″-n-butyryl-$\beta$-D-glucopyranoside (**2**):* yellow powder. – $[\alpha]_D^{29}$ = −24.95° ($c$ = 0.80, $C_5H_5N$). – UV (MeOH): $\lambda(\log\varepsilon)$ = 206 (4.11), 269 (3.61), 342 (3.63) nm. – IR (KBr): $\nu$ = 3425, 2926, 1630, 1384, 1175 cm$^{-1}$. – $^1$H NMR (500 MHz, DMSO) and $^{13}$C NMR (100 MHz, DMSO) data are shown in Table 2. – FAB$^-$-MS: *m/z* (%) = 531 (89) [M–1]$^-$, 299 (100). – HR-TOF-MS: *m/z* = 531.1504 (calcd. 531.1502 for $C_{26}H_{27}O_{12}$, [M–1]$^-$).

*6-O-Ethyl-aucubin (**7**):* white amorphous powder. – $[\alpha]_D^{26} = -121.2°$ ($c = 0.61$, $CH_3OH$). – IR (KBr): $\nu$ = 3429, 2922, 1644, 1340, 1077, 1044, 1014 $cm^{-1}$. – $^1H$ NMR (400 MHz, $CD_3OD$) and $^{13}C$ NMR (100 MHz, $CD_3OD$) data are shown in Table 3. – $FAB^-$-MS: *m/z* = 373 $[M–1]^-$. – HR-TOF-MS: *m/z* = 373.1490 (calcd. 373.1498 for $C_{17}H_{25}O_9$, $[M–1]^-$).

*6-O-Ethyl-epiaucubin (**8**):* white amorphous powder. – $[\alpha]_D^{26} = -75.0°$ ($c = 0.39$, $CH_3OH$). – IR (KBr): $\nu$ = 3425, 2923, 2345, 1642, 1226, 1079, 1049, 1018 $cm^{-1}$. – $^1H$ NMR (400 MHz, $CD_3OD$) and $^{13}C$ NMR (100 MHz, $CD_3OD$) data are shown in Table 3. – $FAB^-$-MS: *m/z* = 373 $[M–1]^-$. – HR-TOF-MS: *m/z* = 373.1500 (calcd. 373.1498 for $C_{17}H_{25}O_9$, $[M–1]^-$).

*Aucubin (**9**):* white amorphous powder. – $[\alpha]_D^{26} = -162.2°$ ($c$ = 0.59, $H_2O$). – $^1H$ NMR (400 MHz, $CD_3OD$) and $^{13}C$ NMR (100 MHz, $CD_3OD$) data are shown in Table 3. – $FAB^-$-MS: *m/z* (%) = 345 $[M–1]^-$.

*Yuheninoside (**10**):* white amorphous powder. – $[\alpha]_D^{29} = -130.9°$ ($c = 0.58$, $CH_3OH$).

*Euphroside (**11**):* white amorphous powder. – $[\alpha]_D^{29} = -106.4°$ ($c = 0.33$, $CH_3OH$).

*Mussaenoside (**12**):* white amorphous powder. – $[\alpha]_D^{26} = -111.1°$ ($c = 0.94$, $CH_3OH$).

*4-Hydroxy-phenylpropenyl-α-*L*-rhamnopyranosyl-(1 → 3)-4-O-feruloyl-β-*D*-glucopyranoside (**13**):* white amorphous powder. – $[\alpha]_D^{28} = -68.0°$ ($c = 0.62$, $CH_3OH$). – UV (MeOH): $\lambda(\log\varepsilon)$ = 204 (4.53), 271 (4.10), 298 (4.10), 327 (4.19) nm. – IR (KBr): $\nu$ = 3431, 2928, 1630, 1603, 1515, 1269, 1035 $cm^{-1}$. – $^1H$ NMR (400 MHz, $CD_3OD$): $\delta_H$ = 1.09 (3H, d, $J$ = 6.2 Hz, H-6‴), 3.40 – 4.52 (9H, m, H of sugar), 3.87 (3H, s, -OMe), 4.44 (1H, d, $J$ = 7.9 Hz, H-1″), 4.87 (1H, m, H-4″), 5.19 (1H, d, $J$ = 1.4 Hz, H-1‴), 6.22 (1H, m, H-8), 6.34 (1H, d, $J$ = 15.9 Hz, H-α), 6.56 (1H, d, $J$ = 15.7 Hz, H-7), 6.72 (2H, d, $J$ = 8.6 Hz, H-3, 5), 6.78 (1H, d, $J$ = 8.2 Hz, H-5′), 7.06 (1H, d, $J$ = 8.2 Hz, H-6′), 7.17 (1H, d, $J$ = 1.6 Hz, H-2′), 7.26 (2H, d, $J$ = 8.6 Hz, H-2, 6), 7.65 (1H, d, $J$ = 15.8 Hz, H-β). – $^{13}C$ NMR (100 MHz, $CD_3OD$): $\delta_C$ = 129.7 (s, C-1), 128.9 (d, C-2), 116.4 (d, C-3), 158.6 (s, C-4), 116.4 (d, C-5), 128.9 (d, C-6), 134.3 (d, C-7), 123.2 (d, C-8), 71.3 (t, C-9), 126.9 (s, C-1′), 111.8 (d, C-2′), 149.8 (s, C-3′), 152.4 (s, C-4′), 116.8 (d, C-5′), 124.6 (d, C-6′), 114.4 (d, C-α), 148.1 (d, C-β), 168.4 (s, C=O), 56.4 (q, -OMe), 103.1 (d, C-1″), 76.1 (d, C-2″), 81.6 (d, C-3″), 70.7 (d, C-4″), 76.2 (d, C-5″), 62.5 (t, C-6″), 103.0 (d, C-1‴), 72.4 (d, C-2‴), 72.1 (d, C-3‴), 73.8 (d, C-4‴), 70.4 (d, C-5‴), 18.4 (q, C-6‴). – $FAB^-$-MS: *m/z* (%) = 633 (30) $[M–1]^-$. – HR-TOF-MS: *m/z* = 633.2197 (calcd. 633.2183 for $C_{31}H_{37}O_{14}$, $[M–1]^-$).

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