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Isolation and Identification of Iridoid Glucosides from *Pedicularis flava* Pall. Growing in Mongolia

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Abstract

We have isolated and structurally elucidated by spectroscopic methods the monoterpenoid iridoid glucosides mussaenoside and euphroside from the aerial parts of the Mongolian medicinal plant *Pedicularis flava* Pall. Euphroside and mussaenoside have been isolated for the first time from this natural source.

Keywords**: **Pedicularis flava; Iridoid; Euphroside; Mussaenoside; Monoterpenoid glucoside

Introduction

Mongolian medicinal plants still offer a great potential for the discovery of new drugs because most of them have not been studied in detail [1,2]. Only a few investigations focused on *Pedicularis flava* Pall. [3]. The flowers and leaves of this plant have been used for the treatment of joint inflammation and poisoning. Moreover, *Pedicularis flava* Pall. has been applied to wound healing. We have isolated the two monoterpenoid iridoid glucosides **1** and **2** (FIG.1) for the first time from *Pedicularis flava* Pall. and assigned their structures.

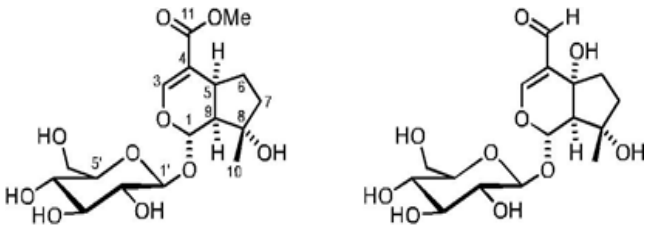

FIG. 1. **Structures of the compounds 1 and 2**.

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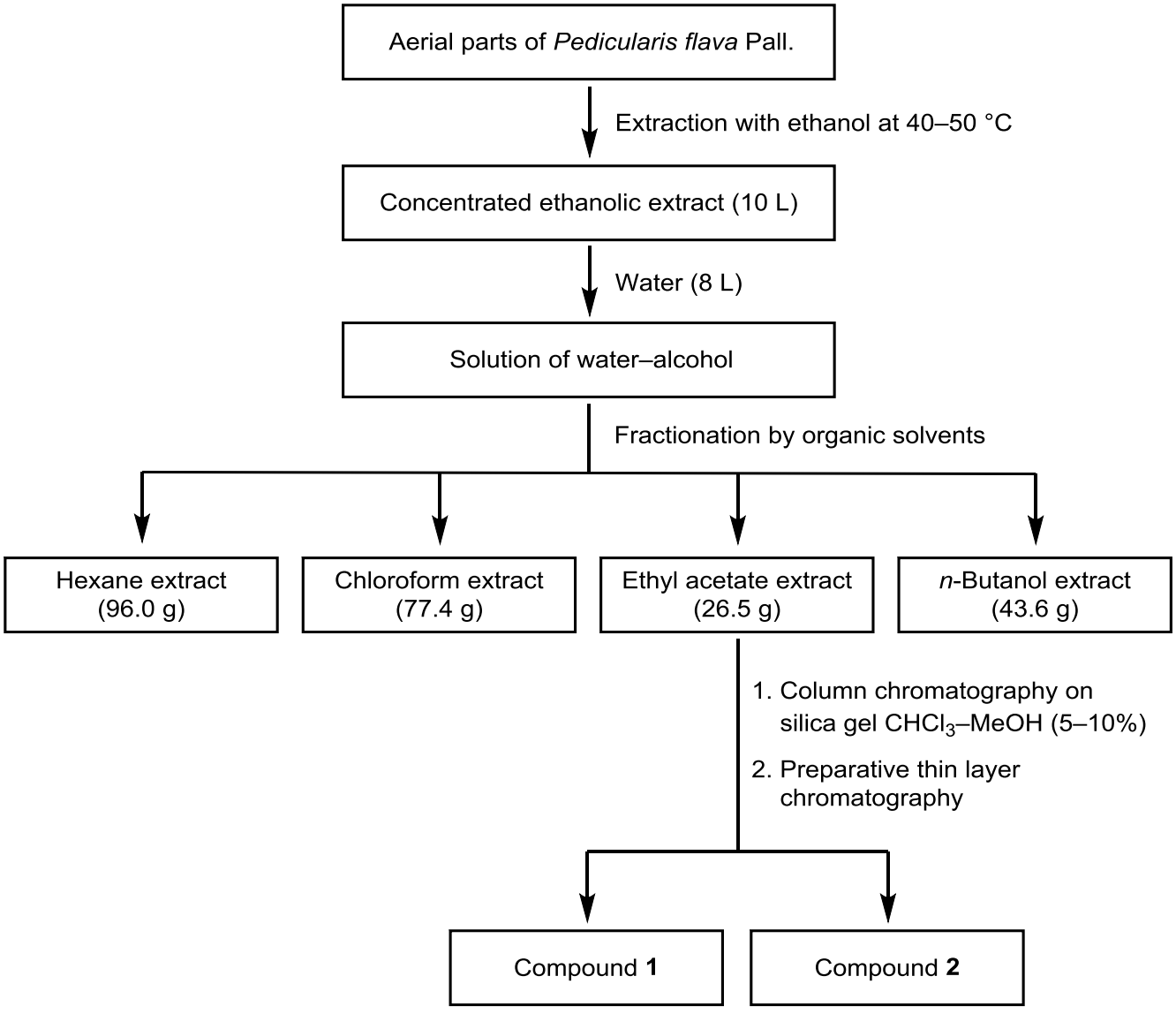
Isolation

The aerial parts of *Pedicularis flava* Pall. (Orobanchaceae) have been collected in Sergelen soum Tuv aimag, Mongolia, during the plant flowering period (August). The botanical assignment was made by Dr. Ch. Sanchir (Institute of Botany, Mongolian Academy of Sciences). The dried and grinded aerial parts of *Pedicularis flava* (12 kg) were extracted with ethanol (72 L) at 40°C to 50°C for 2 h (SCHEME 1). The alcoholic extract was filtered and concentrated using an evaporator at reduced pressure to give 10 L of a concentrated extract. Distilled water (8 L) was poured to the alcoholic extract to give a water–ethanol solution which was fractionated by extraction with solvents of increasing polarity: hexane, chloroform, ethyl acetate, n-butanol. The extracts were dried using Na_2SO_4. Evaporation of the solvents provided the hexane (96.0 g), chloroform (77.4 g), ethyl acetate (26.5 g) and butanolic extracts (43.6 g). Purification of the ethyl acetate extract by column chromatography on silica gel using chloroform–methanol (5% to 10%) as eluent and subsequent preparative thin layer chromatography afforded the compounds **1** and **2**.



SCHEME 1. **Extraction and fractionation of *Pedicularis flava* Pall.**

Results and Discussion

Compound 1 (Mussaenoside)

Compound **1** (mussaenoside) was obtained as an amorphous white powder. For the NMR spectra (500 MHz-^{1}H, 125 MHz-^{13}C and DEPT, and HSQC), CD_3OD was used as solvent. On the basis of ESI-MS (*m/z* = 391.4 $[M+H]^+$ and 408.2 $[M+NH_4]^+$) (FIG. 2) and ^{13}C NMR spectra, compound **1** was assigned the molecular formula $C_{17}H_{26}O_{10}$. The ^{1}H and ^{13}C NMR spectra confirmed that compound **1** is an iridoid monoterpenoid glucoside which by comparison with literature data [4–12] was found to be identical with mussaenoside (TABLE 1).

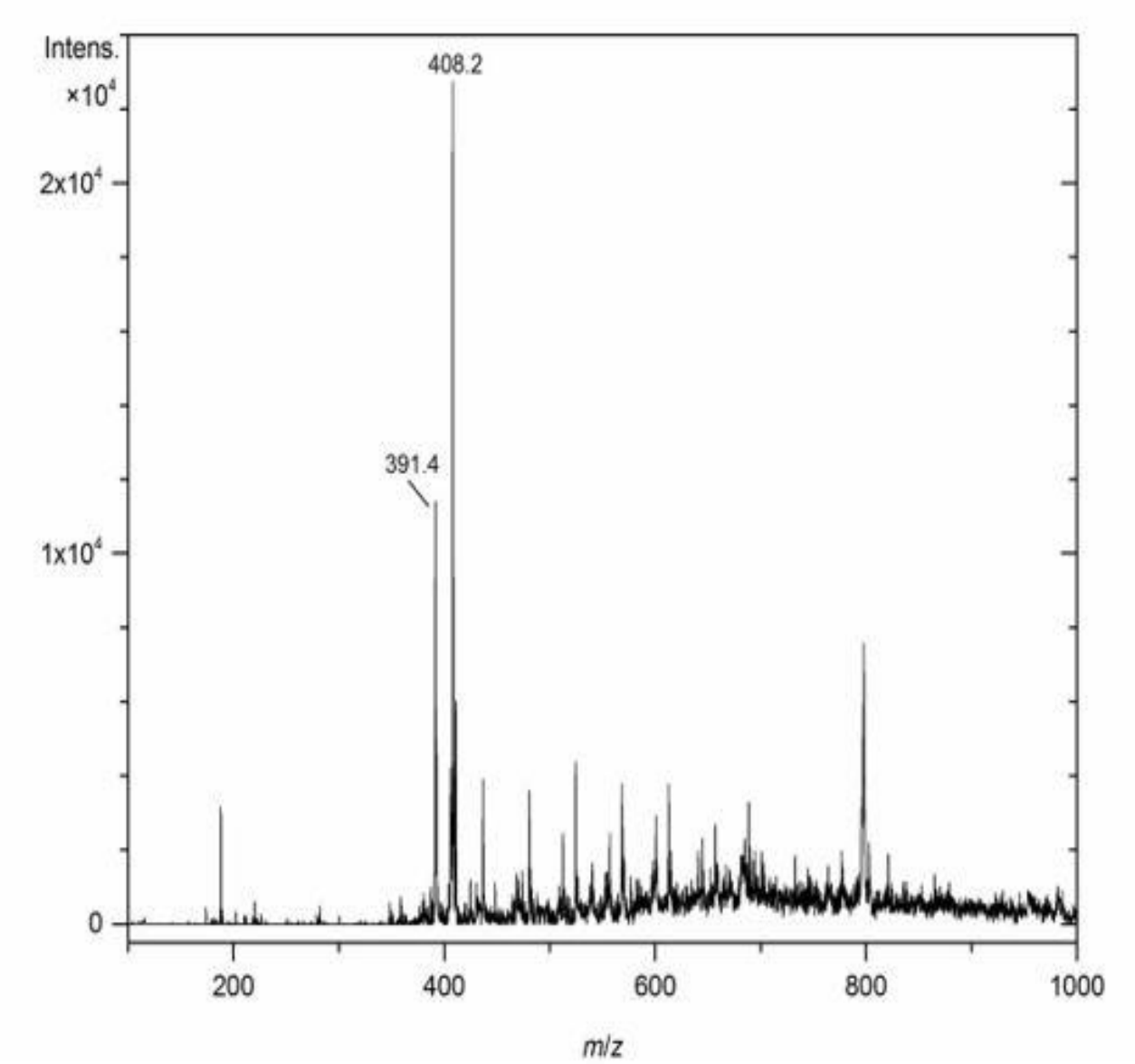


FIG. 2. **ESI-MS (+10 V) of compound 1.**

TABLE 1. **^{1}H and ^{13}C NMR data (CD_3OD) of compound 1 and comparison with mussaenoside.**

	Compound 1 (500 MHz)	**Mussaenoside (400 MHz)**		**Compound 1 (125 MHz)**	**Mussaenoside (100 MHz)**
H	δ (ppm), *J* (Hz)		C	δ (ppm)	
	Aglucone			Aglucone	
1	5.53 (1H, d, *J* = 4.2)	5.45 (1H, d, *J* = 4.2)	1	95.36 CH	95.4 CH
3	7.47 (1H, d, *J* = 1.0)	7.39 (1H, d, *J* = 1.0)	3	152.2 CH	152.1 CH
4	—	—	4	113.40 C	113.4 C
5	2.36 (1H, m)	2.28 (1H, m)	5	32.03 CH	32.1 CH
6	1.5 (2H, m)	1.43 (2H, m)	6	30.74 CH_2	30.8 CH_2
7	1.79 (2H, m)	1.7 (2H, m)	7	40.7 CH_2	40.8 CH_2
8	—	—	8	80.52 C	80.5 C
9	2.29 (1H, dd, *J* = 4.2, 9.2)	2.22 (1H, dd, *J* = 4.2, 9.2)	9	52.31 CH	52.4 CH
10	1.38 (3H, s)	1.32 (3H, s)	10	24.63 CH_3	24.7 CH_3
11	—	—	11	169.40 C=O	169.4 C=O
OMe	3.76 (3H, s)	3.69 (3H, s)	OMe	51.65 CH_3	51.7 CH_3
	Glucosyl			Glucosyl	
1′	4.74 (1H, d, *J* = 7.9)	4.67 (1H, d, *J* = 7.9)	1′	99.81 CH	99.9 CH
2′	3.27–3.45 (1H, m)	3.18 (1H, dd, *J* = 7.9, 9.2)	2′	74.74 CH	74.8 CH
3′	3.27–3.45 (1H, m)	3.24 (1H, dd, *J* = 8.9, 9.2)	3′	78.42 CH	78.4 CH
4′	3.27–3.45 (1H, m)	3.36 (1H, t, *J* = 9.2)	4′	71.72 CH	71.8 CH
5′	3.27–3.45 (1H, m)	3.18 (1H, m)	5′	78.01 CH	78.1 CH
6′	3.71 (1H, dd, *J* = 6.4, 12.0); 3.97 (1H, dd, *J* = 2.0, 12.0)	3.64 (1H, dd, *J* = 6.1,11.9); 3.90 (1H, dd, *J* = 2.2, 11.9)	6′	62.93 CH_2	63.0 CH_2

Compound 2 (Euphroside)

For the NMR spectra (500 MHz-^{1}H, 125 MHz-^{13}C NMR and DEPT, COSY, and HSQC), CD_3OD was used as solvent. A comparison of the ^{1}H and ^{13}C NMR data of compound **2** with those reported for euphroside in the literature [9–15] confirmed that both compounds are identical (TABLE 2).

TABLE 2. **^{1}H and ^{13}C NMR data (CD_3OD) of compound 2 and comparison with euphroside.**

	Compound 2 (500 MHz)	**Euphroside (500 MHz)**		**Compound 2 (125 MHz)**	**Euphroside (125 MHz)**
H	δ (ppm), J (Hz)		C	δ (ppm)	
Aglucone			Aglucone		
1	5.97 (1H, s)	5.85 (1H, br s)	1	95.34	95.3 CH
3	7.41 (1H, s)	7.35 (1H, s)	3	163.09 CH	163.1 CH
4	—	—	4	126.52 C	126.4 C
5	—	—	5	71.24 C	71.3 C
6	2.3 (1H, m); 2.15 (1H, m)	2.25 (1H, m); 1.90 (1H, m)	6	37.8 CH_2	37.6 CH_2
7	2 (1H, m); 1.57 (1H, m)	2.1 (1H, m); 1.50 (1H, m)	7	40.33 CH_2	40.3 CH_2
8	—	—	8	78.85 C	78.9 C
9	2.5 (1H, s)	2.45 (br s)	9	61.46 CH	61.3 CH
10	1.2 (3H, s)	1.2 (3H, s)	10	23.64 CH_3	23.6 CH_3
11	9.3 (1H, s)	9.25 (1H, s)	11	192.53 CHO	192.6 CHO
	Glucosyl			Glucosyl	
1′	4.69 (1H, d, J = 7.9)	4.62 (1H, d, J = 7.8)	1′	99.83 CH	99.8 CH
2′	3.26 (1H, dd, J = 8.0, 9.3)	3.18 (1H, dd, J = 7.8, 9.0)	2′	74.36 CH	74.2 CH
3′	3.43 (1H, m)	3.38 (1H, t, J = 8.5)	3′	78.29 CH	78.3 CH
4′	3.34 (1H, m)	3.34 (1H, t, J = 8.5)	4′	71.65 CH	71.6 CH
5′	3.31 (1H, m)	3.32 (1H, m)	5′	77.43 CH	77.3 CH
6′	3.96 (1H, m); 3.73 (1H, m)	3.85 (1H, dd, J = 2.0, 11.7); 3.65 (1H, dd, J = 6.1, 11.7)	6′	62.81 CH_2	62.7 CH_2

Experimental Section, General

NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR. The chemical shifts δ are given in ppm; the solvent signals were used as reference (^{1}H: δH = 3.35 ppm for residual CD_2HOD, ^{13}C: δc = 49.00 ppm). The coupling constants J are given in Hertz. ESI-MS were recorded on a Bruker-Esquire mass spectrometer with an ion trap detector. Positive and negative ions were detected.

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REFERENCES

1. Medicinal Plants in Mongolia, WHO Regional Office for the Western Pacific. 2013;1-235.
2. Kletter C, Glasl S, Thalhammer T, et al. Traditional Mongolian medicine – a potential for drug discovery. Sci Pharm. 2008;79:49-63.
3. Gonchig E, Erdenebat S, Togtoo O, et al. Antimicrobial activity of Mongolian medicinal plants. Nat Prod Sci. 2008;14 :1-5.
4. Takeda Y, Nishimura H, Inouye H. Two new iridoid glucosides from *Mussaenda parviflora* and *Mussaenda shikokiana*. Phytochemistry. 1977;16:1401-04.
5. Afifi-Yazar F, Sticher O, Uesato S, et al. Ladroside (=6'-caffeoyl-mussaenoside), a new iridoid glucoside from *Veronica officinalis* L. (Scrophulariaceae) and the elucidation of the absolute configuration at C(8) of mussaenoside. Helv Chim Acta. 1981;64:16-24.
6. Damtoft S, Hansen SB, Jacobsen B, et al. Iridoid glucosides from *Melampyrum*. Phytochemistry. 1984;23:2387-89.
7. Otsuka H, Watanabe E, Yuasa K, et al. A Verbascoside iridoid glucoside from *Premna corymbosa* var. *obtusifolia*. Phytochemistry. 1993;32:983-6.
8. Jianmin Y, Shaonong C, Shengping Y, et al. Chemical components from *Craniotome furcata*. Acta Bot Sin. 2001;43:1199-1201.
9. Berg T, Damtoft S, Jensen SR, et al. Iridoid glucosides from *Pedicularis*. Phytochemistry. 1985;24:491-3.
10. Akdemir Z, Çaliş I, Junior P. Iridoids and phenylpropanoid Glycosides from *Pedicularis nordmannia*. Planta Med. 1991;57:584-5.
11. Yuan CS, Zhang Q, Xie WD, et al. Iridoids from *Pedicularis kansuensis* forma *albiflora*. Pharmazie. 2003;58:428-30.
12. Chu HN, Tan NH, Zhang YM. Chemical constituents from *Pedicularis rex* C. B. Clarke. Z. Naturforsch. 2007;62:1465-70.
13. Sticher O, Salama O. Euphroside, A new iridoid glucoside from *Euphrasia salisburgensis* Hoppe. Helv. Chim. Acta 1981;64:78-81.
14. Damtoft S, Rosendal S, Nielsen BJ. ^{13}C and ^{1}H NMR spectroscopy as a tool in the configurational analysis of iridoid glucosides. Phytochemistry. 1981;20:2717-32.
15. Ersöz T, Berkman MZ, Taşdemir D, et al. Iridoid and phenylethanoid glycosides from *Euphrasia pectinata*. Turk J Chem. 2002;26:179-88.