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PHENOLIC GLYCOSIDES FROM *Lespedeza juncea*

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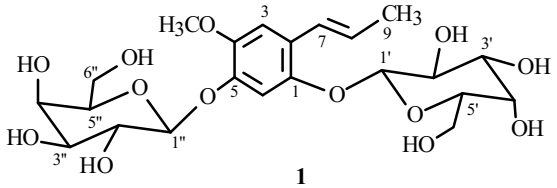
*Two new phenolic glycosides named meoside-A (**1**) and meoside-B (**2**) were isolated from* Lespedeza juncea. *Two compounds were characterized on the basis of 1D and 2D spectral analysis and chemical derivatization.*

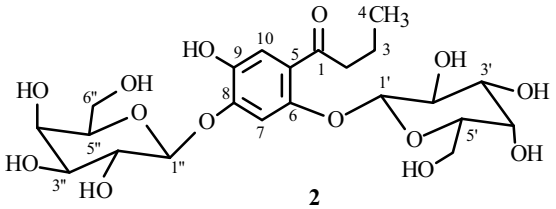
Key words: *Lespedeza juncea*, meoside-A, meoside-B.

Lespedeza juncea of the family *Fabaceae* is used in the traditional medicine of Kashmir, India [1]. The genus *Lespedeza* is a rich source of flavonoids, flavanones, isoflavones, prenylated flavones and flavanones, ethyl caffeate, protocatechuic acid, betulinic acid, β-sitosterol, catechins, daidzein, isoliquiritigenin and alkaloids [2–7], cinnamic acid, ferrulic acid, isorhamnetin, kaempferol, and quercetin [8]. The biological activity in some species of this genus is as an antioxidant and artificial leaf opening substance [9–12]. *Lespedeza juncea,* a woody herb growing at altitudes from 1200–2400 m, has not been investigated for its phytochemical activity so far. As a program of research, we investigated the methanolic extract of the root of the plant and isolated two new phenolic glycosides. We now wish to establish the structure of the two new phenolic glycosides from the above-mentioned plant.

Column and thin layer chromatography of the methanolic extract of the root of *Lespedeza juncea* led to the isolation and characterization of the following two compounds.



1



2

Meoside-A. Analysis of the mass spectrum showed *m/z* at 505 [M+Na], corresponding to the molecular formula $C_{22}H_{32}O_{13}$. The λ_{max} at 281 nm in UV spectrum revealed a substituted benzene moiety. The IR showed a band at 3450 cm^{-1} due to the hydroxyl functionality, at 2929 cm^{-1} due to aromatic - C-H stretching, and at 983 cm^{-1} due to substituted benzene. ^{1}H NMR run at 500 MHz showed two singlets of the aromatic region at δ 7.12 and 6.99; the latter proton is highly shielded by two oxygen functions of two glycosidic moieties. The frequencies at δ 6.32 (1H, dd, J = 2.1, 14.1) and 6.28 are due to the olefinic protons of the side chain. The signals at δ 1.92 and 3.82 revealed the frequencies of methyl and methoxyl groups, respectively. The series of absorption frequencies at δ 4.91 (1H, d, J = 7.4), 3.47 (1H, m), 3.46 (1H, m), 3.42 (1H, m), 3.65 (1H, m), 4.10 (1H, dd, J = 2.1, 12.3), and 3.78 (1H, m) are diagnostic signals of the glucose moiety attached at position-1. The remaining signals at frequencies 4.73 (1H, d, J = 7.1), 3.52 (1H, m), 3.45 (1H, m), 3.59 (1H, m), 3.81 (1H, dd, J = 3.2, 12.1), and 3.43 (1H, m) agreed with another glucose moiety attached to the benzene ring at position-5. ^{13}C NMR showed the C-22 carbon skeleton, and DEPT experiments showed 14 methines, one methyl, one methoxyl, two methylenes of two sugar moieties, and four quaternary carbons. The positions of different groups are assigned by 2D and COSY experiments as shown in Table 1.

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TABLE 1. ^{1}H and ^{13}C NMR (500 MHz, CD_3OD, δ, ppm, J/Hz) Data of Compound **1**

C atom	δ_C	δ_H	COSY	C atom	δ_C	δ_H	COSY
1	146.1			3′	77.7	3.46 (1H, m)	3.47, 3.42
2	130.0			4′	70.1	3.42 (1H, m)	3.46, 3.65
3	119.2	7.12 (1H, s)		5′	78.4	3.65 (1H, m)	4.10, 3.78, 3.42
4	149.4			6′	62.2	4.10 (1H, dd, J = 2.1, 12.3, H-6′α)	3.65
5	148.2					3.78 (1H, m, H-6′β)	3.65
6	100.1	6.99 (1H, s)		1″	102.8	4.73 (1H, d, J = 7.1)	3.52
7	132.1	6.32 (1H, dd, J = 2.1, 14.1)	6.28	2″	71.2	3.52 (1H, m)	4.73, 3.45
8	125.2	6.28 (1H, m)	6.32, 1.90	3″	73.2	3.45 (1H, m)	3.76, 3.52
9	19.2	1.90 (3H, dd, J = 1.5, 7.8)	6.28	4″	69.6	3.76 (1H, m)	3.59, 3.45
10	55.6	3.82 (3H, s)		5″	74.3	3.59 (1H, m)	3.81, 3.76, 3.43
1′	101.6	4.91 (1H, d, J = 7.4)	3.47	6″	62.4	3.81 (1H, dd, J = 3.2, 12.1, H-6″α)	3.59
2′	74.3	3.47 (1H, m)	4.91, 3.46			3.43 (1H, m, H-6″β)	3.59

TABLE 2. ^{1}H and ^{13}C NMR (500 MHz, CD_3OD, δ, ppm, J/Hz) Data of Compound **2**

C atom	δ_C	δ_H	COSY	C atom	δ_C	δ_H	COSY
1	205.6			3′	77.9	3.39 (1H, m)	3.42, 3.41
2	47.2	3.00 (2H, t)	1.68	4′	70.5	3.42 (1H, m)	3.39, 3.32
3	18.2	1.68 (2H, m)	3.00, 1.01	5′	78.7	3.32 (1H, m)	4.11, 3.98, 3.42
4	15.4	1.01 (3H, t)	1.68	6′	62.2	4.11 (1H, dd, J = 3.0, 11.3, H-6′α)	3.32
5	115.7					3.98 (1H, m, H-6′β)	3.32
6	155.8			1″	100.8	4.96 (1H, d, J = 7.2)	3.32
7	98.4	6.88 (1H, s)		2″	72.2	3.32 (1H, m)	4.96, 3.29
8	154.2			3″	75.2	3.29 (1H, m)	3.33, 3.32
9	156.6			4″	70.6	3.33 (1H, m)	3.29, 3.18
10	125.6	6.98 (1H, s)		5″	76.3	3.18 (1H, m)	4.60, 3.98, 3.33
1′	102.6	4.89 (1H, d, J = 7.3)	3.41	6″	61.8	4.60 (1H, dd, J = 3.2, 11.1, H-6″α)	3.18
2′	73.3	3.41 (1H, m)	4.89, 3.39			3.98 (1H, m, H-6″β)	3.18

Meoside-B. Analyzed by mass spectrum *m/z* 521 [M+H], corresponding to molecular formula $C_{22}H_{32}O_{14}$. The λ_{max} at 285 nm in the UV spectrum revealed a substituted benzene system. The IR spectrum revealed absorptions at 3429 cm^{-1} due to the -OH functionality, 2952 cm^{-1} due to aromatic - C-H stretching, and 1725 cm^{-1} due to the carbonyl carbon. ^{1}H NMR swept at 500 MHz showed two aromatic signals of the benzene ring at δ 6.88 and 6.98 at positions 7 and 10, respectively. The triplet, multiplet, and triplet signals at δ 3.00, 1.68, and 1.01 showed a side chain having a $-CH_2-CH_2-CH_3$ pattern. The remaining signals at δ 4.89 (d), 3.41 (m), 3.39 (m), 3.42 (m), 3.32 (m), 4.11 (dd), and 3.98 (m) are due to the glucose attached at position-6. Another series of signals at frequencies 4.96 (d), 3.32 (m), 3.29 (m), 3.33 (m), 3.18 (m), 4.60 (dd), and 3.98 (m) are diagnostic signals of another glucose attached at position-8. ^{13}C NMR showed 22 signals. DEPT experiment analysis showed 12 methines, one methyl, four methylene, and five quaternary carbons. All the positions of protons and substituents were analyzed by 2D and COSY spectroscopy.

EXPERIMENTAL

Melting points are uncorrected and were determined on a BUCHI melting point apparatus. UV spectra were recorded in methanol in nm on a Specord S 100. IR were recorded on a Bruker Vector 22 spectrometer as KBr pellets with absorption given in cm^{-1}. ^{1}H NMR and ^{13}C NMR were run on a 500 MHz Bruker Daltonics instrument using TMS as internal standard. Mass spectra were recorded using Bruker Daltonics electrospray ionization. Column chromatography was run using silica gel (60–120 mesh), TLC were run on silica gel G and fluorescent aluminium TLC using $CHCl_3$ – MeOH solvent. Spots were

visualized on TLC under UV light, ferric chloride, ceric ammonium sulfate, exposure to iodine vapor in an iodine chamber, and also by heating the chromatoplates at 100°C in an oven.

Plant Material. Aerial parts of the plant *Lespedeza juncea* were collected from hilly areas of Shopian, Pulwama (3000–4500 m), Kashmir, India. A voucher specimen was deposited in the herbarium of the institute (No.1031/06).

Extraction and Isolation. Air-dried and coarsely powdered (aerial part) plant material (1.5 kg) was extracted exhaustively with methanol for 64 h. The methanol extract was concentrated under reduced pressure to give 149 g of crude extract. The dried methanolic extract (100 g) was dissolved in the minimum amount of methanol and adsorbed on silica gel to form slurry. The air-dried slurry was subjected to silica gel (60–120 mesh) column chromatography. The column was eluted with different percentages of chloroform and methanol, and the following compounds were isolated.

Meoside-A (1). Colorless powder, mp 183.3°C; UV (MeOH, λ_{max}, nm): 281; IR (KBr, ν, cm^{-1}): 3450 (OH), 2929 (Ar), 1599, 1580, 1523, 1453, 983; ESI-MS: *m/z* 505 [M+H]; ^{1}H, ^{13}C NMR and COSY is given below in Table 1.

Meoside-B (2). White amorphous powder, mp 192.4°C; UV (MeOH, λ_{max}, nm): 285; IR (KBr, ν, cm^{-1}): 3429 (OH), 2952 (Ar), 1567, 1506, 1453, 922; ESI-MS: *m/z* 521 [M+H]; ^{1}H, ^{13}C NMR and COSY is given below in Table 2.

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