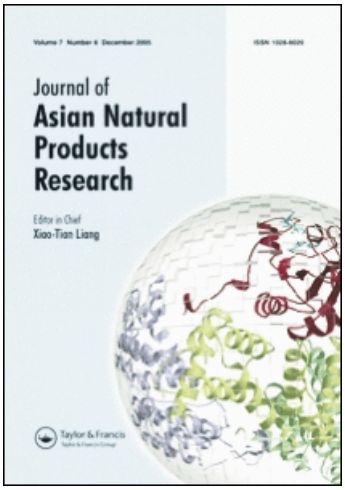

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Caragin, a new isoflavone from *Caragana conferta*

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Caragin, a new isoflavone from *Caragana conferta*

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Caragin (**1**), a new isoflavone, has been isolated from the hexane soluble fraction of *Caragana conferta* along with docosyl-3,4-dihydroxy-*trans*-cinnamate (**2**) and tetracosyl-3,4-dihydroxy-*trans*-cinnamate (**3**) isolated for the first time from this species.

Keywords: *Caragana conferta*; Papilionaceae; isoflavone; Caragin

1. Introduction

The family Papilionaceae comprises of 55 genera and well over 7000 species. The genus *Caragana* has over 80 species out of which 10 species have so far been identified in Pakistan [1]. *Caragana conferta* is a shrub which grows in Asia, Africa, and south east Europe. In Pakistan, it is mainly found in Gilgit and Kashmir valley at an altitude of 7000–12,000 ft above sea level [1]. The plants of genus *Caragana* are used as folk medicine in China and Korea for the treatment of neuralgia, rheumatism, arthritis and hypertension [2]. No phytochemical work has so far been carried out on *C. conferta.* We now report the isolation and structure identification of a new isoflavone named as caragin (**1**) along with docosyl-3,4-dihydroxy-*trans*-cinnamate (**2**) [3] and tetracosyl-3,4-dihydroxy-*trans* cinnamate (**3**) [4], respectively.

2. Results and discussion

Caragin (**1**) was isolated as white needles. The HREIMS established the molecular formula $C_{17}H_{14}O_6$, showing $[M]^+$ peak at *m/z* 314.0790. It gave positive Mg–HCl (reddish) and $FeCl_3$ (greenish brown) color tests. The IR spectrum showed absorption bands due to hydroxyl (3420 cm^{-1}) and carbonyl (1660 cm^{-1}). The UV spectrum showed absorption maximum at 255 nm. The broadband and distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectra of **1** showed 17 carbon signals including two methyl, six methine, and nine quaternary carbons (Table 1). The signal at δ 176.0 was assigned to the conjugated carbonyl while the conjugated olefinic carbon resonated at δ 152.0. The methoxyl carbons were observed at δ 56.5 and 55.3, respectively, while oxygenated aromatic carbons gave signals at δ 160.1, 159.0, 152.5, and 145.1. In ^1H NMR spectrum a singlet of conjugated olefinic proton was observed at δ 7.90. Thus, **1** was deduced to be an isoflavone. In HREIMS the retro Diels–Alder fragments were observed at *m/z* 150.0316 ($C_8H_6O_3$) and *m/z* 164.0473 ($C_9H_8O_3$) revealing the presence of a methoxyl group in ring A and one methoxyl and two hydroxyl groups in ring B. The 1,3,4,5-tetrasubstituted pattern of ring B was confirmed by signals of H-2′ and H-6′ occurring together

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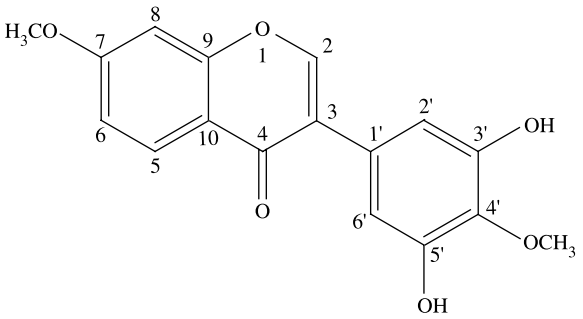

Figure 1. Structure of **1**.

as a singlet at δ 7.63 and the corresponding carbons resonating together to give intense peak at δ 104.8 (Table 1). The signals of shift equivalent C-3′ and C-5′ were also observed together at δ 152.5. The ring A showed an ABX pattern in ^{1}H NMR spectrum revealing the presence of methoxyl group at C-7 [δ 7.47 (1H, d, $J = 8.6$ Hz); δ 6.96 (1H, d, $J = 2.9$ Hz) and δ 6.94 (1H, dd, $J = 8.6$, 2.9 Hz)]. The methoxyl groups at C-4′ and C-7 were further confirmed by HMBC correlations (Table 1). All these data were in complete agreement to the assigned structure of caragin as 3′,5′-dihydroxy-7,4′-dimethoxy-isoflavone (**1**) (Figure 1). Caragin was tested against enzymes lipoxygenase, acetylcholinesterase, and butyrylcholinesterase and showed very weak inhibitory activity.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Gallenkemp apparatus and are uncorrected. IR spectra were measured on a JASCO 302-A spectrophotometer in $CHCl_3$. UV spectra were obtained on a Hitachi UV-3200 spectrophotometer. NMR data were recorded on a Bruker

Table 1. ^{1}H NMR (400 MHz), ^{13}CNMR (100 MHz) spectral data and HMBC correlations for **1** recorded in $CDCl_3$.

Position	δ_H	δ_C	HMBC (H → C)
1	–	–	–
2	7.90 (1H, s)	152.0	C-3, C-4
3	–	124.5	–
4	–	176.0	–
5	7.47 (1H, d, $J = 8.6$ Hz)	130.1	C-6, C-7, C-9
6	6.94 (1H, dd, $J = 8.6$, 2.9 Hz)	113.9	C-5, C-7,
7	–	159.0	–
8	6.96 (1H, d, $J = 2.9$ Hz)	102.6	C-7, C-6, C-9, C-10
9	–	160.1	–
10	–	117.4	–
1′	–	130.0	–
2′	7.63 (1H, s)	104.8	C-1′, C-3′, C-4′
3′	–	152.5	–
4′	–	145.1	–
5′	–	152.5	–
6′	7.63 (1H, s)	104.8	C-1′, C-3′, C-4′
OMe-7	3.82 (3H, s)	55.3	C-7
OMe-4′	4.00 (3H, s)	56.5	C-4′

AV-600 MHz spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts δ are shown in ppm relative to TMS as internal standard and coupling constants J are described in Hz. The HREIMS was recorded on a JEOL JMS-HX-110 mass spectrometer. Silica gel 230–400 mesh (E. Merck) was used for column chromatography. Silica gel plates (Si 60 F_{254}, E. Merck) were used for TLC.

3.2 Plant material

Whole plant of *C. conferta* Benth was collected from Gilgit (Pakistan) and identified by a senior scientist of the National Agriculture Research Center (NARC), Islamabad, Pakistan. A voucher specimen has been deposited in the herbarium of the Department of Botany, University of Karachi (Voucher No. 319).

3.3 Extraction and isolation

The air dried whole plant material (22 kg) was extracted with EtOH (30 Lx 15 days × 3) at room temperature. The extract was evaporated to yield 500 g of crude residue, which was divided into *n*-hexane (80 g), $CHCl_3$ (30 g), EtOAc (8 g), *n*-BuOH (270 g), and H_2O (100 g) soluble fractions. The *n*-hexane soluble fraction was subjected to column chromatography over silica gel eluting with mixtures of *n*-hexane and EtOAc in increasing order of polarity to obtain three major fractions A, B, and C. The fraction B obtained from *n*-hexane and EtOAc (5:5) was again chromatographed over silica gel using *n*-hexane-EtOAc (9:1) as eluent to afford two successive fractions B_A and B_B. Column chromatography of the sub fraction B_B and elution with *n*-hexane–EtOAc (7:3) afforded compound **2** (13 mg) and compound **3** (7 mg) from the top and the tail fractions, respectively. On the other hand, the fraction C obtained from *n*-hexane-EtOAc (4:6) yielded caragin **1** (7 mg).

3.3.1 Caragin (*1*)

White needles. m.p. 246°C. UV λ_{max} (MeOH) nm (log ε): 255 (5.24). IR (KBr) ν_{max} cm^{-1}: 3420, 1660. EI-MS *m/z* 314 (8), 299 (100), 296 (12), 283 (25), 179 (55), 164 (20), 150 (40), 139 (11), and 133 (19). ^{1}H, ^{13}C NMR and important HMBC correlations are shown in Table 1. HREIMS *m/z* 150.0316 ($C_8H_6O_3$), *m/z* 164.0473 ($C_9H_8O_3$), 314.0790 $[M]^+$ (calcd for $C_{17}H_{14}O_6$, 314.0784).

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