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CHEMICAL CONSTITUENTS FROM *DENDROPHTHOE FALCATE*

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abstract: The ethyl acetate extract of the roots and leaves of *Dendrophthoe falcate* yielded apigenin-8-C-β-D (2"-O-β-D-glucopyranosyl)-glucopyranoside. The isolated compounds were characterized by U V, I R, N M R and mass spectral studies.

key words: *Dendrophthoe falcate*; Loranthaceae; flavonoid; c-glucoside.

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Introduction

Dendrophthoe falcate belongs to the family Loranthaceae, also known as "Bandaaka, Vrkshaadani, Vrkshruuhaa" in the Indian Ayurvedic System of Medicine. It is widely distributed throughout in India [1]. This plant is prescribed as a traditional medicine for the treatment of various ailments [1]. *Dendrophthoe falcate* has a wide range of biological activities viz., ulcers, asthma, impotence, paralysis, astringent, narcotic, skin disorder, menstrual troubles, pulmonary tuberculosis, aphrodisiac, astringent, narcotic, consumption, asthma also diuretic [4] for treating wounds [1-5].

The different parts of the plants have been investigated by several workers and found to contain kaemferol, quercetin, myrecitin, and their glycosides are also present [2]. Several cardiac glycosides, flavonoids, and some pentacyclic triterpene present in methanolic leaves extract [3].

Materials and methods

Ultra violet absorption spectrum was recorded on Perkin-Elmer Lambda Bio 20 UV spectrometer. I R spectroscopy was performed on Perkin-Elmer 1710 infrared fourier transformation spectrometer. NMR spectra were recorded on Bruker AVANCE DRX-300(300, 100 Hz). FEBMS was recorded on JEOLSX 1021/DA-6000 mass spectrometer.

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Chemical shifts areshown in δ values (ppm.) with tetramethylsilane (TMS) as an internal reference. Column chromatography was carried using silica gel (60-120 mesh). Chemicals are of analytical-reagent grade were purchased from E-Merck (India).

***Plant material*:** The roots and leaves of *Dendrophthoe falcate* were collected from the rural areas of the Bareilly District in the month of September. Authentication was achieved by the comparison with the herbarium specimen deposited in the herbarium of the faculty of botany, Bareilly College (Rohilkhand University), Bareilly. Fresh or dried plant material can be used as a source for the extraction of secondary plant components. Freshly harvested and dried material more commonly used since old dried material stored for a period may undergo some qualitative changes.

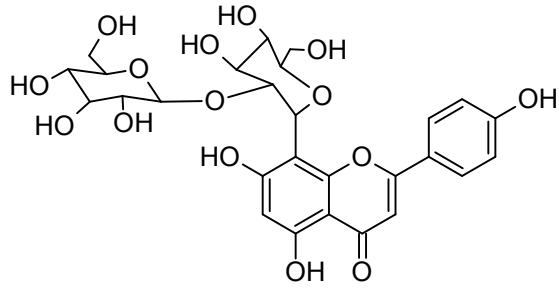
***Extraction and Isolation*:** Roots and leaves were carefully examined and old, insect damaged, fungus-infested were removed. Healthy roots were dried in the laboratory at room temperature in shade. Roots were ground to a fine powder, using a mill. The air-dried coarsely powdered mass of the roots and leaves of *Dendrophthoe falcate* were soxhleted successively with petroleum ether, benzene, chloroform, ethyl acetate and finally with methanol to get their extracts. Only ethyl acetate, extracts were considered for further examination. The extract was column chromatographed separately to yield products. This extract was concentrated to get thick mass. The slurry of each of this mass was made using silica gel in petroleum ether. This slurry was digested over the silica gel column of required weight well settled in petroleum ether. Each column was eluted with different solvents and their mixtures of increasing polarity. Each fraction of these eluents was scrutinized by TLC. The similar fractions were pooled together, which on evaporation yielded different products. The ethyl acetate fraction by eluting the column with petrol ether: methanol (6:4) afforded yellow crystals of flavone glycoside named apigenin-8-C-β-D-(2"-O-β-D-glucopyranosyl)-glucopyranoside (0.98 g).

***Compound CP-1*:** yellow crystals; mp.: 216-218 ^{0}C; UV λ_{max}(nm): (MeOH) 272, 333; (MeOH-NaOMe) 281.0, 401.0; (MeOH:$AlCl_3$) 285.3, 320.1(sh); (MeOH-$AlCl_3$-HCl); 290.0, 318.2(sh), 348.0; (MeOH-NaOAc) 278.1, 308.6, 382.7(sh); (MeOH-NaOAc-H_3BO_3) 279.4, 307.9, 326(sh); ^{1}H NMR (DMSO-d_6) δ: 6.68 (1H, s, H-3), 6.26 (1H, s, H-6), 7.83 (2H, d, J=8.4 Hz, H-2′ 6′), 6.89 (2H, d, J=8.4 Hz, H-3′, 5′), 12.98 (1H, s, C-5 OH), 4.81 (1H, d, J=9.9 Hz, H-1"), 4.08 (1H, d, J=8.4 Hz, H-1‴), 3.40-4.50 (12H, m, Sugar); ^{13}C NMR (DMSO-d_6) δ: 163.43 (C-2), 103.30 (C-3), 181.50 (C-4), 158.6 (C-5), 96.2 (C-6), 159.20 (C-7), 105.10 (C-8), 156.21 (C-9), 105.3 (C-10), 122.4 (C-1′), 116.50 (C-2′/ 6′), 128.80 (C-3′/5′), 162.9 (C-4′), 70.9 (C-1"), 81.6 (C-2"), 78.7 (C- 3"), 71.5 (C-4"), 77.4 (C-5"), 62.9 (C-6"), 105.20 (C-1‴), 75.15 (C-2‴), 76.00 (C-3‴), 71.10 (C-4‴), 75.13 (C-5‴), 61.02 (C-6‴)

Compound CP-1. The compound was obtained as yellow crystals (mp. 216-218 ^{0}C) from ethyl acetate extract by eluting the column with n-hexane: methanol (6:4). Compound gave positive Shinoda test [7] and an alcoholic solution of the compound gave green color with ferric chloride, indicative that the compound was a flavonoid with a free hydroxyl function at C-5 [8]. Its molecular ion peak obtained in its mass spectra at m/z 595 corresponds to the molecular formula $C_{27}H_{30}O_{15}$. The UV spectrum of the compound exhibited the absorption maxima at 272 and 333 nm characteristic of flavonoids [9-10]. The band I (300-380 nm) in MeOH of the compound appear at 333 indicating that the compound belongs to the flavone family unsubstituted at 3- position [9-11]. The addition of NaOMe to methanol solution produced bathochromic shift of band I by 68 nm (from 333 to 401) with an increase in the intensity of absorption, confirming the presence of free 4′-hydroxy group in the compound [9-14]. The UV spectra of the compound showed a single peak at 272 nm indicating that B

ring contains only 4′-OH group. The NaOMe spectrum of the compound was stable for 5 min confirming the absence of free 3-OH group. The addition of NaOAc to MeOH solution of the compound produced an increase in the intensity of absorption indicating the presence of free 7-hydroxy group. The disappearance of band I (300-380 nm) in $NaOAc/H_3BO_3$ spectra of the compound indicated the absence of ortho-dihydroxy groups in both rings. The $AlCl_3$ and $AlCl_3$/HCl produced no significant shift agreed that there is no ortho-dihydroxy group in the compound [9-14].

The ^{1}H NMR spectra of the compound displayed signal at δ 12.98 assignable to a strongly bonded phenolic hydroxyl group [19, 20]. Two two proton doublets observed in its ^{1}H NMR spectrum at δ 7.83 (J=8.4 Hz) and δ 6.89(J=8.4 Hz) were clearly assignable to ring B proton at H-2′, H-6′ and H-3′, H-5′ respectively. The appearance of two doublets and their coupling constants value were further in agreement with the hydroxyl group at C-4′. A singlet appeared at δ 6.68 was assignable to H-3 proton of pyron ring [9-14]. The ^{1}H NMR spectra of the compound exhibited signals at δ 4.81 (J= 9.9 Hz) and 4.08 (J= 8.4 Hz) applicable for two sugar anomeric protons suggesting the presence of β-glucopyranose [10-12]. The structure further supported by its ^{13}C NMR spectrum, which demonstrated a downfield signal at δ 181.50 clearly assignable to carbonyl carbon C-4 of the pyron ring. Another signal observed at δ 103.30 was indicative for C-3. In the ^{13}C-NMR spectra, a signal was observed at δ 70.9 indicating substitution at C-8 position of the aglycone [15]. Further, a signal was observed at δ 81.6 suggested [15] that a glucose unit was attached to C-2″. The three downfield signals appeared at δ158.6, δ 159.2 and δ 162.9 were assigned to C-5, C-7 and C-4′ carbon atoms bearing hydroxyl group. The mass spectrum of the compound exhibited significant peaks at m/z 595 $[M+H]^+$, 433 $[M+H-162]^+$, 415$[M+H-180]^+$, 313 $[M+H-162-120]^+$ and 271 $[M+H-162-162]^+$. The mass fragmentation clearly indicated that two hydroxyl groups are attached to the ring A, while the remaining hydroxyl group is linked with the ring-B at C-4′. The peaks at m/z 433 and 271 confirmed the presence of linkage at C-8. In the mass fragmentation the difference of m/z 120 and m/z 162 indicating that, the second hexose unit is C-glucoside. These data suggested the structure of the compound as apigenin-8-C-β-D (2"-O-β-D-glucopyranosyl)-glucopyranoside. This compound has been isolated for the first time in this genus. This is similar to earlier reported compound vitexin7-O-β-D-glucopyranoside [16].



Apigenin-8-C-β-D (2"-O-β-D-glucopyranosyl)-glucopyranoside.

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