Phytochemical Studies on *Salsola baryosma*

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Summary: Six compounds have been isolated for the first time from *Salsola baryosma* namely, scopoletin (**1**), bergaptol (**2**), daphnoretin (**3**), bergaptol 5-*O*-*β*-D-glucopyranoside (**4**), daphnorin (**5**) and chrysoeriol 7-*O*-*β*-D-glucopyranoside (**6**), respectively. Their structures have been elucidated by spectroscopic techniques.

Introduction

Salsola baryosma Linn. (syn. *S. foetida*) belongs to the family Chenopodiaceae which is widely distributed in Punjab, Northern Gujrat, Rajasthan and Cholistan, where it is used to prepare *sajji*, a crude form of carbonate of soda. The plant is vermifuge and its ashes are applied to itch [1]. Literature survey revealed that a little phytochemical work has so far been carried out on this plant [1, 2]. We now report the isolation and structure elucidation of scopoletin (**1**), bergaptol (**2**), daphnoretin (**3**), bergaptol 5-*O*-*β*-D-glucopyranoside (**4**), daphnorin (**5**) and chrysoeriol 7-*O*-*β*-D-glucopyranoside (**6**), respectively, from the ethyl acetate soluble fraction.

Results and Discussion

Column chromatography of the ethyl acetate soluble fraction of *S. baryosma* resulted in the isolation and characterization of six compounds, including scopoletin (**1**), bergaptol (**2**), daphnoretin (**3**), bergaptol 5-*O*-*β*-D-glucopyranoside (**4**), daphnorin (**5**) and chrysoeriol 7-*O*-*β*-D-glucopyra-noside (**6**). All of these have been reported for the first time from *S. baryosma.*

Experimental

General

Column chromatography was carried out using silica gel of 70-220 and 220-440 mesh. Aluminium sheets precoated with silica gel 60 F_{254} (20×20 cm, 0.2 mm thick; E-Merck) were used for TLC to check the purity of the compounds and were visualized under UV light (254 and 366 nm) followed by ceric sulfate as spraying reagent. Optical rotation was measured on a Jasco DIP-360 digital polarimeter. The UV spectrum was recorded on a Hitachi UV-3200 spectrometer (λ_{max} in nm). IR spectra were recorded on Shimadzu IR-460 spectrophotometer (ν in cm^{-1}). EI-MS, HR-EI-MS, EI-FAB-MS, and HR-FAB-MS spectra were recorded on Jeol JMS-HX 110 spectrometer with data system. The ^{1}H-NMR spectra were recorded on Bruker AMX-400 instruments, using TMS as an internal reference. The chemical shift values are reported in ppm (δ) units and the scalar coupling constants (J) are in Hz.

Plant Material

The whole plant material of *Salsola baryosma* (14 kg) was collected from Cholistan (Distt. Bahawalpur) in July 2003 and identified by Dr. Muhammad Arshad, Plant Taxonomist, Cholistan Institute of Desert Studies, Islamia University Bahawalpur, where a voucher specimen (SB-110) is deposited.

Isolation

The shade dried whole plant (14 kg) was extracted with MeOH (3 × 45L) at room temperature.

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The combined methanolic extract was evaporated under reduced pressure to obtain a thick gummy mass (550 g). It was suspended in water and successively extracted with *n*-hexane, ethyl acetate and *n*-butanol. The ethyl acetate soluble fraction (39 g) was subjected to column chromatography over silica gel eluting with *n*-hexane, *n*-hexane-ethyl acetate, ethyl acetate, ethyl acetate-methanol and methanol in increasing order of polarity. The fractions obtained from *n*-hexane-ethyl acetate (7.5:2.5) were combined and rechromatographed over silica gel using *n*-hexane-ethyl acetate (7.4:2.6) as eluent to obtain scopoletin (**1**) and bergaptol (**2**). The fractions obtained from *n*-hexane-ethyl acetate (5.5:4.5) gave a single spot on TLC, were combined and flash chromatographed over silica gel using the same solvent system to afford daphnoretin (**3**). The fractions obtained from ethyl acetate-methanol (9.5:0.5) were combined and flash chromatographed over silica gel using the same solvent system to obtain bergaptol 5-*O*-β-D-glucopyranoside (**4**). The fractions obtained from ethyl acetate-methanol (9:1) were combined and re-chromatographed over silica gel using ethyl acetate-methanol (8.8:1.2) as eluent to obtain daphnorin (**5**). The fractions obtained from ethyl acetate-methanol (9.5:1.5) were finally purified using chloroform-methanol (7.5:2.5) chrysoeriol 7-O-β-D-glucopyranoside (**6**), respectively.

Scopoletin (1)

Compound **1** (24 mg), obtained as a crystalline solid, m.p. = 202-204 °C; UV (MeOH): λ_{max} (log ε) nm = 227 (3.6), 252 (4.0), 298 (2.6), 341 (4.3); IR ($CHCl_3$) ν_{max} cm^{-1}: 3333 (O-H), 1701 (C=O), 1625-1584 (C=C), 1100 (C-O); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 8.84 (1H, br s, OH), 7.57 (1H, d, J = 9.6 Hz, H-4), 6.89 (1H, s, H-8), 6.82 (1H, s, H-5), 6.24 (1H, d, J = 9.6 Hz, H-3), 3.92 (3H, s, OCH_3); HR-EI-MS showed $[M]^+$ *m/z:* 192.0416 (calcd. for $C_{10}H_8O_4$, 192.0422). The physical and spectral data showed complete agreement with the literature [3].

Bergaptol (2)

Compound **2** (16 mg) was obtained as a creamish solid, m.p. 277-278 °C; UV (MeOH): λ_{max} (log ε) nm = 306 (2.31), 210 (2.76); IR ($CHCl_3$) ν_{max} cm^{-1}: 3404 (O-H), 1705 (C=O), 1611-1573 (C=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.28 (1H, d, J = 9.9 Hz, H-3), 7.32 (1H, s, H-8), 7.75 (1H, m, H-9), 7.82 (1H, d, J = 2.2 Hz, H-10), 8.61 (1H, d, J = 9.9 Hz, H-4); HR-EI-MS, *m/z:* 202.0260 (calcd. for $C_{11}H_6O_4$, 202.0266). The physical and spectral data showed complete resemblance with the reported values [4].

Daphnoretin (3)

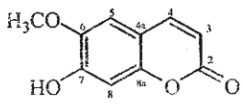
Compound **3** (16 mg), isolated as a crystalline solid, m.p. 244-247 °C; UV (MeOH): λ_{max} (log ε) nm = 212 (4.25), 294 (3.90), 325 (4.01); IR ($CHCl_3$) ν_{max} cm^{-1}: 3480-3090 (O-H), 1722 (C=O), 1608-1500 (C=C); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 8.01 (1H, d, J = 9.5 Hz; H -4′), 7.83 (1H, s, H-4), 7.77-6.95 (5H, m, Ar-*H*), 6.86 (1H, s, H-7, O*H*), 6:35 (1H, d, J = 9.5 Hz; H-3′) 3.83 (3H, s, OCH_3); HR-EI-MS showed $[M]^+$ at *m/z* 352.0575 (calcd. for $C_{19}H_{12}O_7$, 352.0583). The physical and spectral data coincided with the literature values [5-7].

Bergaptol 5-O-β-D-glucopyranoside (4)

Compound **4** (24 mg) was isolated as a crystalline solid, m.p. 254-256 °C; UV (MeOH): λ_{max} (log ε) nm = 304 (2.34), 249 (2.71), 216 (2.72); IR (KBr) ν_{max} cm^{-1}: 3400 (O-H), 1700 (C=O), 1618-1570 (C=C); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 8.64 (1H, d, J = 9.8 Hz, H-4), 7.81 (1H, d, J = 2.0 Hz, H-10), 7.76 (1H, m, H-9), 7.33 (1H, s, H-8), 6.28 (1H, d, J = 9.8 Hz, H-3), 5.67 (1H, d, J = 7.3 Hz, H-1), 4.14-4.66 (6H, H-2′, 3′, 4′, 5′, 6′); HR-MS (+ve FAB) showed $[M+H]^+$ at *m/z* 365.0868 (calcd. for $C_{17}H_{17}O_9$, 365.0872). The physical and spectral data showed complete agreement with those reported in the literature [4].

Daphnorin (5)

Compound **5** (18 mg), was obtained as as amorphous powder m.p. 211–212 °C; $[\alpha]_D$ – 74° (*c* 0.4, CH_3OH); UV (MeOH): λ_{max} (log ε) nm = 335 (4.21), 324 (4.48), 285 (4.99), 227 (4.25); IR (KBr) ν_{max} cm^{-1}: 3480-3090 (O-H), 1722 (C=O), 1608-1500 (C=C); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 7.76 (1H, s, H-4), 7.46 (1H, d, J = 8.5 Hz, H-5) 7.10 (1H, dd, J = 1.8 Hz, 8.4 Hz, H-6), 7.05 (1H, d, J =1.8 Hz, H-8), 6.23 (1H, d, J = 9.5 Hz, H-3′), 7.69 (1H, d, J = 9.5 Hz, H-4′), 7.29 (1H, s, H-5'), 7.19 (1H, s, H-8′), 4.89 (1H, d, J = 7.2 Hz, H-1″), 3.14 (1H, m, H-2"), 3.20 (1H, m, H-3″), 3.34 (1H, m, H-4″), 3.23 (1H, m, H-5"), 3.81,3.41 (2H, m, H-6″), 3.68 (3H, s, OCH_3); HR-MS (-ve FAB) showed $[M-H]^+$ at *m/z* 513.1020 (calcd. for $C_{25}H_{21}O_{12}$, 513.1026). The physical and spectral data resembled the reported values [8].



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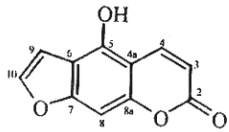

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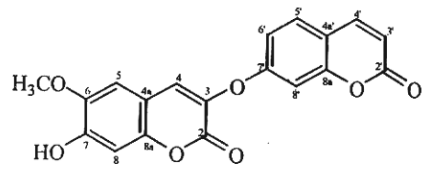

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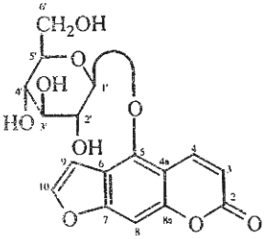

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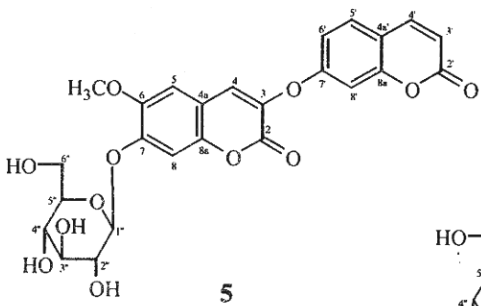

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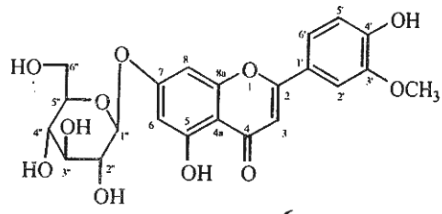

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Chrysoeriol 7-O-β-D-glucopyranoside (6)

Compound **6** (14 mg), a colorless amorphous powder, m.p. 176–179 °C, $[\alpha]_D$ – 35° (*c* 0.05, MeOH); IR (KBr) ν_{max} cm^{-1}: 3452 (O-H), 1714 (C=O), 1648-1555 (C=C); ^{1}H-NMR (CD_3OD, 400 MHz) *δ*: 7.54 (1H, dd, *J* = 8.3, 1.3 Hz, H-6′), 7.50 (1H, d, *J* = 1.3 Hz, H-2′), 6.93 (1H, d, *J* = 8.3 Hz, H-5′), 6.84 (1H, d, *J* = 1.6 Hz, H-6), 6.68 (1H, s, H-3), 6.49 (1H, d, *J* = 1.6 Hz, H-8) and 5.06 (1H, d, *J* = 7.0 Hz, H-1″); HR-MS (+ve FAB) showed $[M+H]^+$ at *m/z* 463.1233 (calcd. for $C_{22}H_{23}O_{11}$, 463.1240). The physical and spectral data showed complete agreement with the reported values [9,10].

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