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NOTE

A New Furocoumarin Glycoside from Aerial Parts of *Pleurospermum brunonis*

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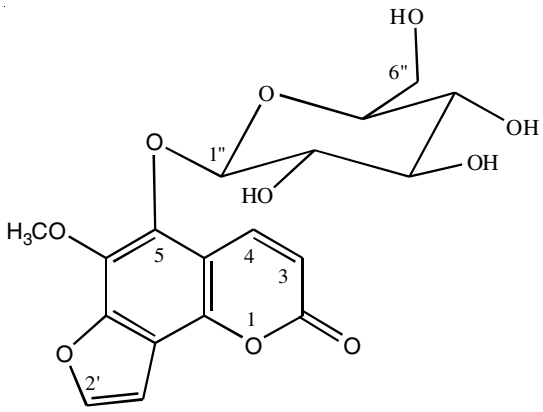
From the ethyl acetate extract of aerial parts of *Pleurospermum brunonis*, a new furocoumarin glycoside 5-O-β-D-glucopyranosyl-6-methoxyangelicin along with ferulic acid and angelicin has been isolated. Structure of isolated compound was elucidated by the analysis of their spectroscopic data and chemical analysis.

Keywords: *Pleurospermum brunonis*, 5-O-β-D-Glucopyranosyl-6-methoxyangelicin, Ferulic acid, Angelicin.

Pleurospermum (Apiaceae) is a genus of perennial, rarely biennial herbs. There are about 50 species confined to north Asia, east Europe and especially diverse in the Himalayan region and west China [1]. *Pleurospermum brunonis is* a perennial herb, 10-15 cm high, found in the temperate regions of Himachal Pradesh and Kashmir at an altitude of 4500-5000 m. The powder of the flowering shoot is mixed with cow's fresh butter and messaged over the entire body to allay fevers, stomatitis and small pox. The dried herb or the garland prepared from the plant is used to protect woolen cloths from the attack of moths and silver fish [2,3]. Coumarins [4-9], saponins [10], flavonoid glycosides [11] and terpenoids [12] have been isolated from various *Pleurospermum* species. Saponins and sapogenins isolated from *P. kamtschatidium* have been reported to possess anti-inflammatory, analgesic, antinociceptive and inhibitory effect on NO, PGE_2 and TNF-α release [13]. There is no previous record of chemical investigation on *P. brunonis*; therefore, the phytochemical examination of ethyl acetate extract of aerial parts of this plant was carried out. The present communication describes the isolation and identification of a new furocoumarin glycoside; 5-O-β-D-glucopyranosyl-6-methoxyangelicin (**1**) along with ferulic acid and angelicin from aerial parts of *P. brunonis*. Structure of isolated compound was elucidated by the analysis of their spectroscopic data and chemical analysis.

The plant material *P. brunonis* was collected from Daggan Dhar (4200-4300 m asl) Bhalessa, District Doda, India, in July, 2010, The plant species were identified by Dr. Sumer Chand, Systematic Botany Division, FRI, Dehradun, India. The voucher specimen (Hr. no. 61) was deposited in the herbarium of Department of Botany, Government P.G. College, Uttarkashi, India.



Structure of 5-O-β-D-glucopyranosyl-6-methoxyangelicin (**1**)

General procedure and detection method: The air-dried and powdered plant material of *P. brunonis* (2 kg) was extracted with light petroleum ether (60-80 °C). The petroleum free mass was sequentially extracted with chloroform, ethyl acetate, acetone and ethanol. Each extract was concentrated under reduced pressure over vacuum evaporator. The ethyl acetate extract (8.5 g) was CC over Si-gel using $CHCl_3$-EtOAc (100→0; 1→1) afforded various fractions. Fraction 1 on repeated CC over Si-gel using gradient elution *n*-hexane-EtOAc (1:1) to give angelicin (89 mg). Fraction 2 on repeated CC over Si-gel on elution with $CHCl_3$-EtOAc (1:3) yielded ferulic acid (29 mg). Fraction 3 on repeated CC over Si-gel eluted with $CHCl_3$:MeOH (2:1) to give compound **1** (21 mg).

5-O-β-D-Glucopyranosyl-6-methoxyangelicin (1): Light yellow amorphous powder; UV (λ_{max}, H_2O): nm 219, 248, 305; IR (KBr, ν_{max}, cm^{-1}): 2910, 1692, 1619, 1582, 1454, 1256, 1061, 1036, *etc.*; (+) FABMS: *m/z*: 395.0934 *etc.*; ^{1}H NMR: (400 MHz, CD_3OD): 6.38 (1H, *d, J* 9.9 Hz, H-3), 8.58 (1H, *d, J* 9.9 Hz, H-4), 7.85 (1H, *d, J* 2.3 Hz, H-2') 7.12 (1H, *d, J* 2.3 Hz, H-3') 4.66 (1H, *d, J* 7.8 Hz H-1") 3.55 (1 H, *t, J* 7.8, Hz, H-2") 3.46 (1H, *d, J* 7.8, Hz, H-3"), 3.49 (1H, *d, J* 7.6 Hz, H-4"), 3.38 (1H, *ddd, J* 7.6, 5.2, 2.4 Hz, H-5"), 3.76 (1H, *dd, J* 5.2, 11.8 Hz, H-6a"), 3.83 (1H, *dd, J* 2.4, 11.8 Hz, H-6b"), 3.88 (3H, *s*, -OCH_3); ^{13}C NMR (100 MHz, CD_3OD): 162.98 (*s,* C-2), 113.40 (*d,* C-3), 141.76 (*d,* C-4), 143.09 (*s,* C-5), 136.73 (*s,* C-6), 149.54 (*s,* C-7), 117.41 (*s,* C-8), 143.38 (*s,* C-9), 112.80 (*s,* C-10), 147.85 (*d,* C-2'), 104.12 (*d,* C-3'), 106.49 (*d,* C-1"), 74.76 (*d,* C-2"), 76.82 (*d,* C-3"), 70.11 (*d,* C-4"), 79.09 (*d,* C-5"), 61.76 (*t,* C-6"), 59.01 (*q,* C_6-OCH_3).

Acid hydrolysis of compound 1: Compound **1** (5 mg) was refluxed with 5 % aqueous HCl (5 mL) at 80 °C for 3 h. After cooling, the reaction mixture was neutralized with $AgNO_3$. The aqueous layer after concentration under reduced pressure was subjected to PC using BuOH-AcOH-H_2O (5:1:4) with authentic sugars. The sugar was identified as D-glucose.

The ethyl acetate extract of aerial parts of *P. brunonis* on repeated CC over Si-gel afforded a new furanocoumarin glycoside; 5-O-β-D-glucopyranosyl-6-methoxyangelicin (**1**) along with ferulic acid and angelicin. The structure of ferulic acid and angelicin was determined by direct comparison of their spectral data with the reported values [14,15].

Compound **1** a light yellow amorphous powder, was found to have molecular ion peak at *m/z* 395.0942 in the positive HRFABMS spectrum (calc. for $C_{18}H_{19}O_{10}$; 395.0978). The IR spectrum showed characteristic absorption band for carbonyl group at 1699 cm^{-1}. Its UV absorption maxima at 219, 248 and 305 nm were similar to that of 5,6-dioxygenated angelicin skeleton [16]. The ^{1}H NMR and ^{13}C NMR spectra of **1** were similar to those of furanocoumarins. The ^{13}C NMR spectrum of **1** showed 18 carbon signals out of which carbon signals at δ 104-163 due to the 11 carbons of the angular furocoumarin nucleus, one signal for anomeric carbon of the glucose, five carbon signals at δ 60-80 due to the sugar moiety and one signal for methoxy carbon at δ 59.01. The assignment proton and carbon signals were made by DEPT, ^{1}H-^{1}H COSY and HSQC experiments.

The ^{1}H NMR spectrum showed characteristic signals of a disubstituted furan ring at δ 7.84 (*d, J* 2.3 Hz, H-2') and 7.12 (*d, J* 2.3 Hz, H-3') and an AX type spin system at δ 6.38 (*d, J* 9.9 Hz, H-3) and 8.58 (*d, J* 9.9 Hz, H-4), which was confirmed by ^{13}C chemical shifts of carbon atoms at δ 147.85 (C-2') 104.12 (C-3') and 113.40 (C-3), 141.76 (C-4). In addition to these signals ^{1}H NMR spectra also displayed presence of methoxy group at δ 3.88 and an anomeric proton at δ 4.66 (*d, J* 7.8 Hz, H-1") along with signals assignable to sugar protons. The presence of methoxy group and sugar moiety was confirmed by ^{13}C shifts of methoxy carbon at δ 59.01 and anomeric carbon at δ 106.49. On acid hydrolysis with HCl compound **1** afforded D-glucose. The β-orientation of sugar was determined from the value of coupling constant (*J* 7.8 Hz) of anomeric proton. Absence of aromatic protons in ^{1}H NMR spectrum suggested that both C-5 and C-6 positions are substituted. The HMBC spectrum displayed $^3J_{CH}$ correlation of anomeric proton at δ 4.66 with the carbon signal at δ 143.09 (C-5) and $^3J_{CH}$ correlation of H-4 proton (δ 8.58) with C-5. The methoxy protons at δ 3.88 showed $^3J_{CH}$ correlation with C-6 carbon at δ 149.55. These data unambiguously established that the glucose and methoxy group was attached at C-5 and C-6 position of furocoumarin nucleus, respectively. Accordingly, the structure of **1** was deduced as 5-O-β-D-glucopyranosyl-6-methoxyangelicin.

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