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BIS-COUMARINS FROM *EDGEWORTHIA GARDNERI*

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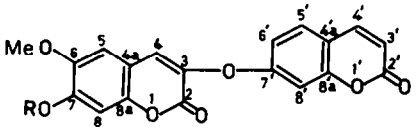
Key Word Index—*Edgeworthia gardneri*; Thymelaeaceae; *bis*-coumarin; daphnoretin; 7-*O*-acetyl daphnoretin.

Abstract—7-*O*-Acetyl daphnoretin has been isolated from *Edgeworthia gardneri* together with daphnoretin. This is the first report of the isolation of the former from a natural source.

Two *bis*-coumarins daphnoretin (**1**) [1], $C_{19}H_{12}O_7$ ($[M]^+$ *m/z* 352), mp 244–245° (ethanol) and **2**, $C_{21}H_{14}O_8$, ($[M]^+$ 394), mp 230–232° (methanol) have been isolated from the ethyl acetate extract of *Edgeworthia gardneri*. Compound **2** showed UV absorption [λ_{max}^{EtOH} nm (log ε): 212 (4.25), 294 (3.90) and 325 (4.01)] typical of 7-alkoxy coumarins [2]. The IR spectrum of this compound suggested the presence of a phenolic acetate (1760 cm^{-1}) and an α,β-unsaturated δ-lactone (1725 cm^{-1}). The 400 MHz ^1H NMR spectrum of the compound revealed the presence of three vinylic protons, two of which appeared as doublet at δ6.20 (1H, *d*, *J* = 9.5 Hz) and 7.65 (1H, *d*, *J* = 9.5 Hz) and one as singlet at δ7.20. It also recorded signals for one acetoxy methyl group (δ2.40, 3H, *s*), one methoxyl function (δ3.80, 3H, *s*) and five aromatic protons [δ6.71 (1H, *s*), 6.94 (1H, *s*), 7.38 (1H, *d*, *J* = 9.5 Hz), 6.73 (1H, *d*, *J* = 9.5 Hz) and 6.62 (1H, *s*)].

The structure of the compound **2** was confirmed as 7-*O*-acetyl daphanoretin from its ^{13}C NMR spectrum. During this investigation the ^{13}C NMR spectrum of daphnoretin, which had not been reported earlier, has also been studied. Three carbonyl groups could be clearly seen [δ168.29 (O<u>C</u>OMe), 160.28 (C-2 or C-2') and 158.71 (C-2' or C-2)] in addition to one methoxyl (56.44) and eighteen aromatic carbons (Table 1) for 7-*O*-acetyl daphnoretin.

Compound **2** was found to be identical to the acetylation product of daphnoretin. This is the first report of the isolation of 7-*O*-acetyl daphnoretin from a natural source.



1 R = H
2 R = Ac

EXPERIMENTAL

Plant material. Stem bark of *E. gardneri* Meissn. was collected from Darjeeling, West Bengal, India. A voucher specimen (No. Eg) has been preserved in our laboratory.

Isolation of daphnoretin and 7-O-acetyl daphnoretin. Air-dried, powdered stem bark (2.5 kg) was extracted with petrol for 48 hr. The defatted material was then extracted with EtOAc for 72 hr. The EtOAc extract was concd and chromatographed over silica gel (BDH, 60–120 mesh). The C_6H_6–EtOAc (4:1) eluates gave a

Table 1. ^{13}C NMR spectral data of daphnoretin (**1**) in DMSO-d_6 and 7-*O*-acetyldaphnoretin (**2**) in $CDCl_3$ (δ in ppm)

C	1	2
2	161.10*	160.28*
3	136.85	140.03
4	132.02	129.31
4a	115.52†	116.61†
5	103.94	105.73
6	151.54	148.99
7	154.60	155.40
8	110.56	111.95
8a	145.08‡	142.12‡
2'	160.81*	158.71*
3'	111.31	114.24
4'	146.84	142.79
4'a	114.98†	115.30†
5'	130.98	126.71
6'	105.09	108.97
7'	156.13	156.54
8'	114.55	115.17
8'a	148.58‡	145.66‡
OMe	57.20	56.44
O<u>C</u>OMe	—	20.58
O<u>C</u>OMe	—	168.28

*†‡Values may be interchanged.

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solid which on repeated crystallization from MeOH gave 7-*O*-acetyl daphnoretin (**2**), yield 0.004%, mp 230–232°. IR ν_{max}^{KBr} cm^{-1}: 1760, 1725, 1620, 1500, 1210, 1190, 840; MS *m/z*: 394 $[M]^+$, 352, 324, 179 and 89.

Daphnoretin (**1**) was isolated from the C_6H_6–EtOAc (1:1) eluates and purified by crystallization from EtOH, yield 0.24%, mp 244–245°; MS *m/z*: 352 $[M]^+$, 324, 296, 191, 179 and 89.

Acetylation. Daphnoretin (50 mg) was refluxed with a mixture of Ac_2O (10 ml) and pyridine (2 ml) at 100° for 6 hr. The reaction mixture was kept at room temp. for 1 hr and then poured onto crushed ice with continuous stirring. The solid ppt was crystallized from $CHCl_3$–MeOH (1:1), yield 75%, mp 232°. The product was found to be identical to naturally occurring 7-*O*-acetyl daphnoretin (**2**) from mmp, co-TLC and superimposeable IR spectra.

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FLAVONE *C*-GLYCOSIDES OF *ALMEIDEA GUYANENSIS*

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Key Word Index—*Almeidea guyanensis*; Rutaceae; isoswertisin; 6,8-di-*C*-arabinosylapigenin; 2″-*O*-xylosyl-8-*C*-arabinosylgenkwanin; 6-*C*-glucosyl-8-*C*-arabinosylgenkwanin.

Abstract—From the stem and the root bark of *Almeidea guyanensis* were identified isoswertisin, 6,8-di-*C*-arabinosylapigenin and two new compounds 2″-*O*-xylosyl-8-*C*-arabinosylgenkwanin, and 6-*C*-glucosyl-8-*C*-arabinosylgenkwanin.

We have previously reported flavonoids and alkaloids from *Almeidea guyanensis* Pulle [1, 2]. The present paper describes the isolation and identification of other flavonoids of stem bark.

Two flavonoids were isolated and identified as isoswertisin (**1**) and 6,8-di-*C*-arabinosylapigenin (**2**) by their chromatographic and spectral properties (UV) [3], MS of PM derivatives [4, 5], their hydrolysis products and by direct comparison of TLC and HPLC of free compounds and TLC of PM derivatives with authentic samples. Compounds **3** and **4** showed UV spectra and diagnostic shifts [3] characteristic of 7-*O*-substituted apigenin derivatives. Their mobility in water on PC and the results of the acid hydrolysis (extraction was possible with *n*-butanol but not with ether) suggested their *C*-glycosidic nature [6]. Compound **3** gave on acid hydrolysis xylose what is in agreement with *O*-glycosyl-*C*-glycosylflavone. MS of PM **3** showed peaks at the following *m/z*: 646 $[M]^+$ (0, 23), 471 $[M-175]^+$ (22, 4), 455 $[M-191]^+$ (7), 341 $[M-305]^+$ (100). This fragmentation is characteristic of PM *O*-pentosyl-8-*C*-pentosylflavone [5, 7].

PM **3**, by acid hydrolysis, gave compound with fragmentation in MS identical with that of the hydrolysis product of PM 2″-*O*-glucosyl-8-*C*-arabinosylgenkwanin, what shows a free hydroxyl in the 2″-position. By acid hydrolysis then permethylation, PM **3** gave a compound identical with PM 8-*C*-arabinosylgenkwanin [8] (TLC and MS). Furthermore, after acid hydrolysis and purification by PC in BAW, **3** gave a compound that was identical with 8-*C*-arabinosylgenkwanin (UV, diagnostic shifts and cochromatography). Compound **3** was thus identified as 2″-*O*-xylosyl-8-*C*-arabinosylgenkwanin.

The MS of PM **4** showed peaks at the following *m/z*: 704 $[M]^+$, 689 $[M-15]^+$ (19), 673 $[M-31]^+$ (100) and a series of characteristic peaks of 6-*C*-hexosyl-8-*C*-pentosylapigenin with losses from the $[M]^+$ at $[M-119]^+$ (3), $[M-131]^+$ (9), $[M-145]^+$ (1), $[M-163]^+$ (29), $[M-175]^+$ (32), $[M-189]^+$ (18) [4]. Furthermore,