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A PERSICOGENIN 3′-GLUCOSIDE FROM THE STEM BARK OF *PRUNUS AMYGDALUS*

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Key Word Index—*Prunus amygdalus*; Rosaceae; stem bark; persicogenin 3′-glucoside; NOE, 2D HOMCOR spectra.

Abstract—A new flavanone glycoside, persicogenin 3′-glucoside (5,3′-dihydroxy-7,4′-dimethyoxyflavanone 3′-glucoside) has been characterized from the stem bark of *Prunus amygdalus*.

INTRODUCTION

Prunus species have been reported as antipyretic, refrigerant, useful against thirst, leprosy and leucoderma [1, 2]. *Prunus amygdalus* nuts have shown antiinflammatory activity [3]. Kaempferol, quercetin-3-*O*-diglucoside and 8-methoxykaempferol-3-sophoroside from pollen [4] and flavones from the seed coat [5] have been reported. Here, we report on a novel persicogenin glycoside from the ethanolic extract of the stem bark of *P. amygdalus*.

RESULTS AND DISCUSSION

The ethanolic extract of the stem bark of *P. amygdalus* on column chromatography gave **1** which was found to have M_r of 478 inferred by the presence of a peak at *m/z* 501 $[M + Na]^+$ and 339 $[M + Na - 162]^+$ in the + ve ion FAB-mass spectrum recorded in thioglycerol matrix with NaCl. UV absorption of **1** showed λ_{max}^{MeOH} at 287 and 333 nm which shifted bathochromically on adding $AlCl_3$ indicating a free hydroxyl at C-5 [6]. Compound **1** was insoluble in aqueous Na_2CO_3 and gave a purple colour with conc HNO_3 suggesting a methoxyl group at C-7 [7]. Acidic hydrolysis of **1** gave an aglycone **1a**, mass spectrum *m/z* 316. The ^{1}H NMR spectrum of **1a** revealed a phenolic, a chelated phenolic, two methoxyls and an ABX system corresponding to three aliphatic protons of C-2 and C-3. The two protons (C-6 and C-8 H) in the ring A showed a *meta* spin spin splitting. The signal pattern of protons in the ring B indicated an ABC pattern. A series of NOE difference spectra recorded on the diacetate (**1a**Ac) confirmed the assignment of substituents on the flavanone skeleton. The sugar in the aqueous hydrolysate of **1** was found to be glucose.

In the ^{1}H NMR spectrum of **1**, the protons of sugar moiety resonated at a very low field around 5 ppm, probably owing to the anisotropic effect of the C ring. The position of the β-linked glucose ^{1}H–^{1}H HOMCOR confirmed it at δ4.95 (J = 9.0 Hz) at 3′ of the flavanone was inferred by NOE observed between 2′ of the genin and anomeric proton in **1**. The ^{13}C signals in **1** and **1a** were assigned by comparison [8]. Thus the structure of **1** is persicogenin 3′-glucoside (5,3′-dihydroxy-7,4′-dimethoxyflavanone 3′-glucoside).

EXPERIMENTAL

Mps: uncorr. FAB-MS was measured by JEOL AX-505 mass spectrometer. ^{1}H NMR recorded at 270 and 500 MHz and ^{13}C NMR at 68 MHz. Chemical shifts on a δ(ppm) scale with TMS as an int. standard. GLC of the trimethylsilyl derivative (prepared as described [9]) was carried out on a Shimadzu-GC-8A and recorded by Shimadzu Chromatopac C-R6A. The conditions were as follows: column 3% OV-101 Chromosorb W; column temp. 150–220° 3 min^{-1}, injection temperature, 250°, carrier gas N_2, 1 g cm^{-2}.

Extraction and isolation of flavonoid **1**. The bark (1 kg) of *Prunus amygdalus* collected from the Horticulture Research Centre, Srinagar (Garhwal) was extracted with hot EtOH (2 l × 3). The ethanolic extract was evapd to give a residue (120 g) which was partitioned between *n*-BuOH and H_2O (1 l each). The BuOH soluble fraction was concd *in vacuo* to afford a residue (50 g) which on CC over silica gel ($CHCl_3$–MeOH–H_2O, 9:1:0.1) gave **1** (60 mg).

Compound **1**. Needles from MeOH, mp 204–205°, $[\alpha]_D^{24}$ − 37.24° (DMSO; *c* 0.114), gave a red colour with Mg/HCl. The UV λ_{max}^{MeOH} nm 287, 333; MeOH + $AlCl_3$ 309, 365 (no change on adding HCl). ^{1}H NMR (DMSO-d_6): δ4.95 (1H, *d*, J = 9 Hz). ^{13}C NMR (DMSO-d_6): δ196.7 (C-4), 167.4 (C-5), 163.1 (C-3′), 162.7 (C-9), 149.1

(C-4'), 146.2 (C-7), 130.6 (C-6'), 120.5 (C-1'), 113.7 (C-2'), 112.1 (C-5'), 102.5 (C-10), 99.7 (C-1''), 95.3 (C-6), 93.7 (C-8), 79.0 (C-2), 76.9 (C-5''), 76.9 (C-3''), 73.0 (C-2''), 69.7 (C-4''), 60.6 (C-6''), 55.8 (OMe-4'), 55.6 (OMe-7) and 41.9 (C-3).

Acidic hydrolysis of compound **1**. Compound **1** (25 mg) in 1 M HCl–50% EtOH was refluxed for 2 hr and the reaction mixture was diluted. The ppt. was collected by filtration and purified by recrystallization from MeOH to afford needles, **1a**, mp 162–164°. EI-MS (*m/z*): 316 $[M]^+$ (100%), 315 $[M-H]^+$, 193, 166, 150, 137, 81, 69. ^{1}H NMR ($CDCl_3$): δ12.0 (1H, *s*, OH-5), 7.25 (1H, *s*, H-2'), 7.05 (1H, *d*, H-6'), 6.92 (1H, *m*, H-5'), 6.08 (1H, *d*, H-6), 6.05 (1H, *d*, H-8), 5.77 (1H, *s*, OH-3'), 5.33 (1H, *dd*, H-2), 3.95 and 3.85 (3H each, *s*, 2 × OMe), 3.04 (1H, *dd*, H-3β), 2.81 (1H, *d*, H-3α). ^{13}C NMR ($CDCl_3$): δ196.0 (C-4), 168.0 (C-5), 164.1 (C-3'), 162.8 (C-9), 147.0 (C-4'), 145.9 (C-7), 131.5 (C-6'), 118.2 (C-1'), 112.7 (C-2'), 110.7 (C-5'), 103.1 (C-10), 95.1 (C-6), 94.2 (C-8), 79.0 (C-2), 56.1 (OMe-4'), 55.7 (OMe-7), 43.2 (C-3). Diacetate (**1a**Ac), mp 129–131°, ^{1}H NMR ($CDCl_3$): δ7.25 (1H, H-6'), 7.20 (1H, *s*, H-2'), 7.0 (1H, *d*, H-5), 6.42 (1H, *d*, H-6), 6.28 (1H, *d*, 8H), 5.4 (1H, *dd*, H-2), 3.82 (3H, *s*, OMe-4'), 3.80 (3H, *s*, OMe-7), 3.0 (1H, *dd*, H-3β), 2.72 (1H, *dd*, H-3α), 2.40 (3H, *s*, Ac-5), 2.35 (3H, *s*, Ac-3').

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