

chromatographed on a column with polyamide by elution with toluene and increasing quantities of MeCOEt and MeOH. The solvents used for TLC on polyamide were (A) toluene–petrol (bp 100–140°)–MeCOEt–MeOH (30:90:2:1.5) and (B) toluene–petrol (bp 100–140°)–MeCOEt–MeOH (60:30:10:15). Prep. TLC was done on Si with solvent (C) (toluene–MeCOEt, 9:1.) A sample of dihydrowogonin (from bud exudate of sweet cherry tree [14]) was partially methylated according to Ref. [15] by addition of Me₂SO₂ to a soln in EtOH with NaHCO₃. The reaction product forms colourless crystals, mp 101° (lit. [9], 97°). Apigenin 7-methyl ether was identified by direct comparison with an authentic marker.

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A FLAVANONE GLYCOSIDE FROM *PRUNUS CERASOIDES*

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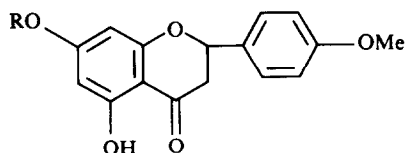
Key Word Index—*Prunus cerasoides*; Rosaceae; seeds; naringenin 4'-methyl ether 7-xyloside.

Abstract—During a phytochemical investigation of the seeds of *Prunus cerasoides*, a new flavanone glycoside, naringenin 4'-methyl ether 7-xyloside, was characterized.

Prunus cerasoides, commonly known as Padam in Hindi, is reputed to possess therapeutic value in its seeds and stem [1, 2]. No previous chemical studies have been carried out on the seeds of this plant. The present paper reports the isolation and characterization of a new flavanone glycoside, naringenin 4'-methyl ether 7-*O*-β-D xylopyranoside (1) from the seeds of *P. cerasoides*.

The UV spectrum and diagnostic shifts [3] of 1 were characteristic of a 7,4'-di-*O*-substituted naringenin. 1 was confirmed as an *O*-glycoside by its ¹H NMR spectrum [4] in CDCl₃ which exhibited six

aromatic protons (H-2', H-6', H-3', H-5', H-6' and H-8), methoxyl protons and a multiplet for sugar protons along with other protons (H-2 and H-3). Acid hydrolysis of 1 with 7% ethanolic sulphuric acid yielded naringenin 4'-methyl ether (2) (mp, mmp, IR, UV, ¹H NMR, MS, co-chromatography, acetylation, demethylation) and xylose (co-PC and GLC; TMS ether). Periodate oxidation showed the consumption of 2 mol periodate with the liberation of 1 mol formic acid per 1 mol of the glycoside indicating the presence of a sugar in the monosaccharide pyranose form. 1 showed a positive bathochromic shift with aluminium



1 R = Xylose

2 R = H

chloride, indicating a free hydroxyl at C-5. Methylation of **1** followed by acid hydrolysis yielded naringenin 5,4'-dimethyl ether (mp, mmp and co-TLC), further confirming xylose at the 7-position. Hydrolysis with almond emulsin gave xylose.

EXPERIMENTAL

Isolation and purification. Air-dried and powdered seeds (2 kg) of *Prunus cerasoides* D. Don. from Pratap Nursery and seed stores, Dehradun (India), were exhaustively extracted $\times 3$ with EtOH. The total EtOH extract was concd (100 ml) and poured into H₂O (500 ml). The H₂O soluble fraction was extracted with EtOAc to give **1** which was purified over a Si gel column (elution with petrol-EtOAc, 1:1) and crystallized as yellow needles from MeOH (yield 750 mg).

Naringenin 4'-methyl ether 7-O-xyloside (1). Mp 140–142°(d), C₂₁H₂₂O₉ ([M]⁺ 418), (found: C, 60.28; H, 5.30; requires C, 60.30; H, 5.25%). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 289, 325 (sh); + AlCl₃ 311; + NaOAc 289, 330 (sh). IR $\nu_{\text{max}}^{\text{KBr}}$ 3450 (br), 2900, 2868, 2850, 1680, 1601, 1500, 1470, 1380, 1300, 1270, 1170, 1125, 1030, 900, 825, 822. ¹H NMR (90 Hz, CDCl₃) δ 7.85 (2H, d, *J* = 8.5 Hz, H-2' and H-6'); 6.94 (2H, d, *J* = 8.5 Hz, H-3' and H-5'); 6.84 (1H, d, *J* = 2.5 Hz, H-8), 6.42 (1H, d, *J* = 2.5 Hz, H-6), 5.98 (1H, d centred at 5.25, H-2), 2.80 (d, *J* = 17 Hz, H-3) (eq), 3.32 (q, *J* = 2 Hz, H-3) (ax), 3.95 (3H, s, X OMe), 3.85 (m, sugar protons). MS at *m/z*: 418 [M]⁺, 403

[M – Me]⁺, 400 [M – H₂O]⁺, 390 [M – CO]⁺, 311 [M – C₇H₅O]⁺, 310 [M – C₇H₆O]⁺, 123 [M – C₁₄H₁₅O₇]⁺. TLC (Si gel *R_f* 0.82 (C₆H₆-EtOAc, 1:1), 0.58 (CHCl₃-EtOAc, 1:1). PC (Whatman No. 1) *R_f* 0.55 (BAW, 4:1:5), 0.20 (HOAc-HCl-H₂O, 6:1:2).

Naringenin 4'-methyl ether (2). Mp 193–194°, TLC, *R_f* 0.60 (C₆H₆-EtOAc, 1:1).

Acetylation and acetyl percentage determination of 2. **2** (50 mg) was acetylated (Ac₂O-pyridine) by the usual method, mp 138–140°. The percentage of acetyl groups in the product was determined. (Found: COMe, 23.34%; calc. for C₁₆H₁₂O₅ (COMe)₂; 23.24%.)

Determination of the methoxyl group in 2. The methoxyl group in **2** was determined by the method of Zeisel's as described by Belcher *et al.*[5]. (Found: OMe, 10.86%; calc. for C₁₅H₁₁O₄ (OMe), 10.84%.)

Enzymatic hydrolysis of 1. **1** (20 mg) was hydrolysed with almond emulsin at 40° for 24 hr. Xylose was detected by PC.

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