extract, dried under red. pres. and re-dissolved in H_2O, was chromatographed on a cellulose column using H_2O as eluant. The first eluate yielded needles of **1**, which were purified by TLC on cellulose with H_2O as solvent (a band at R_f 0.65).

Identification of 6-C-glucosylnaringenin (**1**). UV λ_{max}^{MeOH} nm: 328sh, 291, 226; NaOMe: 327, 249; $AlCl_3$: 360, 310; $AlCl_3$–HCl: 364, 309; NaOAc: 328, 285sh, 254; NaOAc–H_3BO_3: 330, 293. MS (chalcone PM) 70 eV, direct inlet, *m/z* (rel. int. %): 546 $[M]^+$ (4.5), 385 (2.3), 371 $[M-175]^+$ (100), 370 (6), 257 $[M-189]^+$ (2.5), 355 $[M-191]^+$ (3.5), 341 $[M-205]^+$ (12), 328 $[M-218]^+$ (4.8), 251 (5), 237 (4.2), 236 (4), 235 (5.3), 223 (11), 209 (4.5), 207 (13), 205 (5.7), 193 (5.6), 179 (3.5), 161 (27), 151 (6.8), 147 (6.5), 134 (6.8), 133 (13), 121 (16). TLC: Polyamide (Macherey & Nagel, DC 6) H_2O–MeOH–MeCOEt–Ac_2CH_2 (10:6:2:1) (R_f: 0.67). Cellulose: H_2O (0.65), 15% HOAc (0.76), 30% HOAc (0.78), 60% HOAc (0.83). Si gel: EtOAc–MeOH–H_2O (21:4:3) (0.75).

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THE OCCURRENCE OF FLAVANONES IN THE FARINOSE EXUDATE OF THE FERN *ONYCHIUM SILICULOSUM*

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Key Word Index—*Onychium siliculosum*; Pteridophyta; frond exudate; chalcone isomerization; 5-hydroxy-7, 8-dimethoxyflavanone; 5-hydroxy-6, 7-dimethoxyflavanone.

Abstract—The yellow farina on fertile pinnules of *Onychium siliculosum* is composed of 2′,6′-dihydroxy-4′-methoxychalcone and 2′,6′-dihydroxy-4,5′-dimethoxychalcone. Heating of the crude extract brings about isomerization to pinostrobin and to 5-hydroxy-7,8-dimethoxyflavanone and 5-hydroxy-6,7-dimethoxyflavanone, respectively. The latter flavanone, recently reported as a constituent of this fern, is thus not a natural product.

Onychium siliculosum (Desv.) C.Chr. is a gymnogrammoid fern which according to Hooker [1] grows in the Himalayas and on the Malayan peninsula and islands. The fertile pinnules of its fronds bear a conspicuous yellow farina on the under surface. Two flavonoids, namely 2′,6′-dihydroxy-4′-methoxychalcone (**1**) and 2′,6′-dihydroxy-4′,5′-dimethoxychalcone (**2**) have been reported previously as 'constituents' of this fern (*Onychium auratum* Kaulf.) [2] without mention of the fact that they form the yellow farina (cf. ref. [3]). In the course of our chemotaxonomic studies on gymnogrammoid ferns we wanted to isolate chalcone **2** (pashanone) to have it available as an authentic marker. The orange-yellow farina was dissolved with acetone from one frond of *Onychium siliculosum* and the yellow solution was dried onto polyamide in an oven. The material became rather pale and after CC, it yielded a comparatively large amount of non-polar flavanone but only a small proportion of chalcone. One of the flavanones was readily identified as pinocembrin 7-methyl ether (pinostrobin, **3**). Two unknown flavanones, **4** and **5**, appeared as a twin-pair of spots that almost overlap. Since no reasonable amount of the required chalcone had been obtained in this first attempt, another tall fertile frond was rinsed with acetone. The quasi-crystalline material obtained after evaporation of the acetone was dissolved in warm benzene and applied directly to a column with polyamide. Now this time hardly any flavanone was obtained, whereas chalcones could be recovered in good quantities. Hence, in the first case heating of the flavonoid in the oven must have caused formation of flavanone from the chalcones present in the farina, this assumption being supported by the reduction in chalcone **1** in favour of the flavanone **3**. Therefore the residue from the crystallization of 2',6'-hydroxy-4',5'-methoxychalcone (**2**) was heated to 180°; the chalcone practically disappeared, whereas the above-mentioned pair of flavanones, **4** and **5**, appeared. The two components were separated by prep. TLC on silica. The small amounts isolated could not be crystallized and hence no mp could be determined, but the samples were chromatographically pure, so UV and mass spectra could be recorded.

The UV spectra of the two compounds are identical ($\lambda_{\max}^{\mathrm{MeOH}}$ nm: 345, 292; + NaOH 370, 292; no shift with NaOAc), except for the reaction with AlCl$_3$, which gave UV $\lambda_{\max}$ at 400 and 316 nm for **4**, but 390, 316 nm for **5**. The mass spectra of **4** and **5** are identical, too, even the intensities of the fragments generally agreeing; and the same fragments are present also in the mass spectrum of chalcone **2**. The data for **4** are m/z (rel. int.): 300 $[M]^+$ (58) (flavanone with 1 hydroxyl and 2 methoxyls [4]), 299 $[M-1]^+$ (7), 257 (3), 223 $[M-77]^+$ (13) (unsubstituted B-ring), 196 $[M-104]^+$ (70), 181 (100; A-ring with 1 hydroxyl and 2 methoxyls), 168 (24), 167 (15), 153 (49), 125 (25), 104 (15), 103 (18), 77 (26), 69 (31). With the assumption that the flavanones **4** and **5** originated from the chalcone **2** by closure of the C ring, they should be 5-hydroxy-7, 8-dimethoxyflavanone and 5-hydroxy-6, 7-dimethoxyflavanone. The differences in the UV shifts in the presence of aluminium chloride indicate that in **4** the methoxyl group is situated at C-8 ($\Delta\lambda$ 55 nm) and in **5** it is situated at C-6 ($\Delta\lambda$ 45 nm). The chromatographic behaviour is also in favour of these structures: **4** appears as a brownish spot in UV$_{366}$ at slightly higher R_f than **5**, which is dark and remains dark on spraying with 'Naturstoffreagenz A' (**4** turns brown). The same effects have been observed with cryptostrobin or 5,7-dihydroxy-8-methylflavanone (higher R_f, brownish spot turning dull yellow; $\Delta\lambda$ with AlCl$_3$ 19 nm) versus strobopinin or 5, 7-dihydroxy-6-methylflavanone (lower R_f, dark spot turns brown; $\Delta\lambda$ AlCl$_3$ 3 nm) [5], for their methylation products (5-hydroxy-7-methoxy-8-methylflavanone: slightly higher R_f, brown spot turns dull yellow; $\Delta\lambda$ AlCl$_3$ 53 nm; 5-hydroxy-7-methoxy-6-methylflavanone: lower R_f, dark spot remains dark; $\Delta\lambda$ AlCl$_3$ 3 nm; Wollenweber, unpublished results), and also for some novel flavanones isolated from the farina of *Cheilanthes argentea* [6]. In total the data reported establish that **4** is 5-hydroxy-7,8-methoxyflavanone and **5** is 5-hydroxy-6,7-methoxyflavanone. The correctness of the structure deduced for flavanone **4** was confirmed by direct comparison with the synthetic product (see Experimental), which is identical in every respect.

5-Hydroxy-6,7-methoxyflavanone has been reported recently as a 'constituent' of *Onychium siliculosum* [7]. The authors believed it to be a novel natural flavanone and proposed the trivial name onysilin. However, this flavanoid was first found as a constituent of aerial parts of *Chrysothamnus nauseusus* (Asteraceae) [8]. From this plant it was obtained as an impure oily product only and its structure was deduced from IR and mass spectral data. 5-Hydroxy-7, 8-methoxyflavanone would indeed be a new natural flavanone. As a synthetic product it has been described at least twice before [9, 10]. We obtained it by partial methylation of dihydrowogonin with dimethyl sulphate. Apigenin-7-methyl ether (genkwanin) was found in trace amounts. Some further trace constituents of the farina could not be identified due to lack of material.

In both previous phytochemical studies on *Onychium siliculosum* [2, 7] the workers used powdered fern fronds. Hence it escaped their attention that the compounds they isolated came from the farinose frond exudate. In [2] the material was extracted with light petrol and the two chalcones **1** and **2** were isolated. In ref. [7] an ethanol extract was treated with chloroform and water. This should not necessarily cause isomerization of the chalcones, but possibly this had occurred during the drying of the plant material or of the crude extract. It is noteworthy that these authors also isolated pinostrobin (**3**), whereas flavanone **4** was not encountered, although they processed 2.5 kg (!) of plant material. Our experiments demonstrate that 2',6'-hydroxy-4'-methoxychalcone can form 5-hydroxy-7-methoxyflavanone, and 2',6'-hydroxy-4',5'-methoxychalcone (pashanone) can form 5-hydroxy-7,8-methoxyflavanone and 5-hydroxy-6,7-methoxyflavanone, e.g. on heating, either of crude extracts or of isolated chalcones. It has been reported earlier that 2',4'-hydroxy-6'-methoxychalcone on heating to 200° yielded 7-hydroxy-5-methoxyflavanone (alpinetin) by cyclization [11]. It may also be mentioned here that 2',3',4',6',4-pentahydroxychalcone, the aglycone of carthamin, on hydrolysis of this glycoside, isomerizes to 5,7,8,4'-hydroxyflavanone (isocarthamidin) and 5,6,7,4'-hydroxyflavanone (carthamidin) [12]. Curiously enough, the reverse reaction has been observed recently with some flavanones from *Pityrogramma pallida*: 7-hydroxy-5-methoxyflavanone, 7-hydroxy-5-methoxy-6-methylflavanone, and 5,7-methoxy-6-methylflavanone on heating yielded the corresponding chalcones [13].

We have compared older extracts of several samples of *Onychium siliculosum* with freshly prepared solutions of the yellow farina of some specimens and found that the flavanones **3–5** are absent from the latter. Hence we believe that these three flavanones must be regarded as artefacts and not as natural flavonoids.

EXPERIMENTAL

Fronds of *Onychium siliculosum* were collected near Darjeeling and made available by S. P. Khullar, Chandigarh, India. From a tall frond weighing *ca* 4.5 g, *ca* 270 mg exudate material (6% frond dry wt) could be dissolved by rinsing with Me$_2$CO. After evaporation of the Me$_2$CO the remainder was dissolved in warm C$_6$H$_6$. This soln was 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 Me_2SO_2 to a soln in EtOH with $NaHCO_3$. 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 ^{1}H NMR spectrum [4] in $CDCl_3$ 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, ^{1}H 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