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FLAVONOIDS OF *PHILYDRUM LANUGINOSUM*

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Key Word Index—*Philydrum lanuginosum*; Philydraceae; Monocotyledonae; flavonoids; syringetin 3-*O*-β-D-galactopyranoside; kaempferol; isorhamnetin; quercetin; syringetin; glucosides; galactosides; glucuronides; chemotaxonomy; flavonoid nuclear magnetic resonance.

Plant. Philydrum lanuginosum Banks et Soland ex Gaertn., Philydraceae. *Source*. Bribie Island, Queensland, Australia; collected in full flower. Voucher reference is No. 4217, Botany Department, University of Queensland, Brisbane.

Previous work. The plant lacks alkaloids [1]. Little is known of the chemistry of the family: Bate-Smith [2] reported cyanidin, delphinidin, and cinnamic acids from *Orthothylax glaberrima*. Webb and his colleagues [1] could find neither alkaloids nor saponins in *Helmholtzia glaberrima*.

Present Work. Air-dried plants were extracted with MeOH–H_2O (5:1). Removal of solvent left a residue from which polyphenolics were removed with boiling water. EtOAc extraction of the water yielded the polyphenolic fraction which was separated on a column of Polyamide SC-6 using MeOH–H_2O mixtures. Monitoring and final purifications were achieved using TLC on Polyamide DC-6·6 and solvents A-D, Silica Gel-G and solvent E, and Avicel and solvent F. Solvents: (A) C_6H_6–MeOH: butanone–H_2O (55:20:23:2); (B) H_2O–EtOH–*n*-BuOH–HOAc (75:10:13:2); (C) H_2O–butanone–acetone–formic acid (60:30:9:1); (D) butanone–H_2O–acetone–formic acid (50:40:5:5); (E) *n*-butyl acetate–butanone–HOAc–H_2O (60:25:12:3); and (F) 10% HOAc in H_2O. Solvent (E) resolves glucoside/galactoside pairs in three runs. Solvents (C) and (D) resolved the glucuronide mixture.

The major flavonoid yielded an unknown (to us) aglycone, galactose, and a small amount of glucose. The glycoside gave a UV spectrum characteristic of a flavonol-3-*O*-glycoside [3]. NMR of the trimethylsilylated aglycone: 7·56 δ (*s*, 2H, $\underline{H}$-2′, $\underline{H}$-6′); an ABq (J_{meta} = 2 Hz) at 6·46 δ (1H, $\underline{H}$-8) and 6·18 δ (1H, $\underline{H}$-6); and 3·89 δ (*s*, 6H, 3′-$OC\underline{H}_3$ and 5′-OMe). Symmetrical placement of the B-ring protons at C-2′ and C-6′ is required by the appearance of the 7·56 δ resonance as a singlet [3]. NMR of the TMS-glycoside: 3·4 δ (6H, complex, monohexoside) and 5·47 δ (*d*, J = 7 Hz, 1H, anomeric H in β-D-conformation). The aglycone is thus, 5,7,4′-trihydroxy-3′,5′-dimethoxyflavonol; the glycoside is the corresponding 3-*O*-β-D-galactopyranoside. A small amount of the 3-*O*-β-D-glucopyranoside also seems to exist. The aglycone, known as syringetin, was synthesized by Heap and Robinson [4] who recorded m.p. 224–226° for the tetraacetate. The tetraacetate of the present compound had m.p. 226–228° which also agrees with the data of Pardhasaradhi and Sidhu [5].

Other minor flavonoid constituents were isolated and identified by standard, hydrolytic, chromatographic, and UV methods. These included a kaempferol 3-*O*-bioside (trace), isorhamnetin 3-*O*-glucoside, isorhamnetin 3-*O*-galactoside, an isorhamnetin 3-*O*-bioside which gave glucose and galactose upon hydrolysis, quercetin 3-*O*-glucoside, quercetin 3-*O*-galactoside, quercetin 3-*O*-rutinoside, and a trace of a syringetin 3-*O*-bioside.

A second group of flavonoids was observed which had very low R_f values (in A and B) but were resolved by the use of acidic solvents (C and D). These compounds resisted acidic hydrolysis but were readily split with β-glucuronidase into glucuronic acid and the aglycones seen above: kaempferol, quercetin, isohamnetin, and syringetin. A small amount of quercetin galacturonide may also be present as judged by its R_f and UV behaviour which were very close to that of the glucuronide. Also, the unknown failed to respond to β-glucuronidase. All members of this group migrated toward the anode in electrophoretic runs at pH 5·7 and 3 kV. UV data show all these to be 3-*O*-glucuronides (with a 3-*O*-galacturonide subject to confirmation).

The finding of syringetin 3-*O*-β-D-galactoside and 3-*O*-β-D-glucuronide marks the first reports of these compounds in nature. Syringetin has been found before but it still ranks as one of the rarer flavonols. Other sources are: flowers of *Lathyrus pratensis* [6], needles of *Larix* species [7,8], heartwood of *Soymida febrifuga* [5], and epigeal parts of *Limnanthes* species [9].

The occurrence of syringetin and isorhamnetin glycosides in *Philydrum* may have potential in helping to elucidate taxonomic relationships of Philydraceae. Close examination of other members of the family as well as members of Pontederiaceae would be of interest. Cronquist [10] states that, "The Pontederiaceae and Philydraceae stand off sharply from the rest of the Liliales and from each other". Cronquist [10] also mentions the resemblance of *Philydrum* to Commelinaceae. Hamann [11] has concluded that Philydraceae is most closely related to Pontederiaceae and that these two families are best treated as a peripheral subgroup of the Liliales. The only chemical hint which we have on the subject is the observation by Bate-Smith that members of both families have the capacity to form the 3′,4′,5′-trihydroxylated B-ring as evidenced by the occurrence of leucodelphinidin in *Orthothylax* (Philydraceae) and in *Eichornia* and *Pontederia* (Pontederiaceae).

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