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FLAVONOIDS AND GALLIC ACID DERIVATIVES FROM *PELTIPHYLLUM PELTATUM**

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Key Word Index—*Peltiphyllum peltatum*; Saxifragaceae; kaempferol, quercetin, and myricetin 3-*O*-monosides; arabinosides, rhamnosides; glucosides; myricetin 3-*O*-xyloside; tannins; gallylglucose derivatives.

Plant. Peltiphyllum peltatum (Torr.) Engl., collected at Sixmile Creek at Illinois River Road, Siskiyou National Forest, OR, U.S.A., voucher in UBC. This is a monotypic genus in Saxifragaceae, subfamily Saxifragoideae, tribe Saxifrageae which occurs in northern California and southwestern Oregon [1]. *Previous work.* Jay and Lebreton [2] found kaempferol, quercetin, myricetin, leucodelphinidin, leucocyanidin, and ellagic acid in acid hydrolyzed extracts of leaves. Frohne [3] reported the presence of arbutin while Gibbs [4] recorded the presence of raphides and a negative test for cyanogenetic compounds.

Present work. As part of our study of polyphenols of the Saxifragaceae we undertook an examination of *Peltiphyllum peltatum*, endemic to Oregon and northern California. The only flavonoids present in the plant were kaempferol, quercetin, and myricetin in agreement with Jay and Lebreton [2]. The monoglycoside fraction contained the 3-*O*-arabinosides, 3-*O*-rhamnosides, and 3-*O*-glucosides of each of these and the 3-*O*-xyloside of myricetin. The diglycoside fraction consisted of kaempferol and quercetin 3-*O*-rutinosides along with small quantities of a diglycoside of each which gave arabinose and xylose upon hydrolysis. The order of attachment of the sugars was not determined. In addition a trace of a myricetin 3-*O*-diglycoside was also seen. None of the flavonol 3-*O*-triosides, flavonol glycoside gallates or flavonol 4'-*O*-glycosides, found in other members of the tribe Saxifrageae [5–9], was present in this plant.

A fraction of very polar material was obtained which gave a strong test for gallic acid derivatives. The mixture was resolved into five apparently homogeneous compounds. Acid hydrolysis of three of these (tannins 1–3) gave only glucose and gallic acid suggesting simple esters. These compounds had R_f 0.31, 0.35 and 0.60, respectively, using 6% HOAc on paper. Comparison with the data of Haslam [10] suggests that tannins 2 and 3 might be trigallylglucoses while tannin 1 is a monogallylglucose. Tannin 4 gave neither glucose nor gallic acid on hydrolysis while tannin 5 gave glucose but not gallic acid. We did not observe ellagic acid in any of the hydrolyses.

The Saxifrageae was considered by Engler [11] to consist of 24 genera and as such represented the largest tribe in his treatment of the family. The tribe is richly represented in northwestern North America and was a logical starting point for our chemotaxonomic study of the family. To date detailed structural information has been compiled on members of *Tellima* [5–7,9], *Heuchera* [8], *Elmera* [12], *Jepsonia* [13], *Chrysosplenium* [14], *Tolmeia* [15], and now *Peltiphyllum*. Certain types of compounds have been encountered which have promise for comparative studies. All taxa so far examined have a rich array of flavonol 3-*O*-monoglycosides and 3-*O*-diglycosides whereas flavonol 4'-*O*-glycosides have been found only in *Tellima*. Flavonol 3-*O*-triglycosides have been found in *Heuchera* and the very closely related *Elmera*. Flavonol 3-*O*-gallylglycosides have been found in *Tellima*, *Heuchera*, *Jepsonia* and may be present in *Tolmeia* as well. In addition, other gallic acid derivatives, e.g. gallotannins, ellagitannins, have been found in several taxa. Structures have been established for some of these derivatives from *Tellima* and *Heuchera*.

The only genus whose position in the tribe can be challenged on the basis of phenolic chemistry is *Chrysosplenium* which synthesizes a wide variety of *O*-methylated flavonols [16]. Work in our laboratory [14] with *C. tetrandrum* has shown the presence of *O*-methylated compounds but also a group of kaempferol and quercetin 3-*O*-mono- and 3-*O*-diglycosides very similar to those present in the other members of the tribe.

EXPERIMENTAL

Plant material was extracted with MeOH and the extract evaporated to dryness. Extraction of residue with hot H_2O and extraction of aq. soln with EtOH gave the polyphenols. These were subjected to column chromatography using LH-20 and increasing amounts of MeOH in water. Individual fractions were evaporated to dryness and subjected to partition chromatography on Avicel using EtOAc/light petroleum. Further purifications were accomplished by TLC using Polyamide DC-6.6 and solvent systems described in ref. [8]. UV studies were performed according to Mabry *et al.* [17]. Tannins were obtained from the LH-20 column with 100% MeOH and separated by partition column chromatography and purified using TLC as above. Hydrolyses were done with trifluoroacetic acid at 100°.

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* Number 6 in the series, "Chemotaxonomic Studies of the Saxifragaceae". For number 5 see ref. [9].

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FLAVONOID EXUDATIONS IN FARINOSE FERNS

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Key Word Index—*Adiantum sulphureum*, *Cheilanthes*, *Notholaena*; Polypodiaceae; exudates; flavonoid methyl ethers.

Plants. Adiantum sulphureum Kaulf.; *Cheilanthes albomarginata* C. B. Clarke, *C. bullosa* Kze., *C. grisea* Blanford, *C. rufa* D. Don.; *Notholaena candida* (Mart. & Gal.) Hook, *N. schaffneri* (Fourn.) Underw. var. *nealleyi* (Seaton) Weatherby, *N. standleyi* Maxon. *Source.* Botanic Garden of Concepcion, Chile (A.s.), Kew Herbarium (Ch.), natural habitat in Texas (N.). *Previous work.* Flavonoids from *C. farinosa* [1, 2], *C. longissima* [3] (nom. val.?); chalcones, dihydrochalcones and flavones in *Pityrogramma* sp. (lit. cit. in [4]).

Present work. Leaves, pinnules or only fragments were rinsed with acetone to dissolve the farina deposited on under surface. The components were identified by cochromatography with authentic substances on polyamide and silica gel (comp. [5]).

Adiantum sulphureum. The farina of this species consists mainly of 2′,6′-diOH, 4′-OMe chalcone (to which yellow coloration is due) and 2′,6′-diOH,4′-OMe dihydrochalcone with trace amounts of galangin and galangin 7-methyl ether (izalpinin) and still unknown minor compounds.

Cheilanthes albomarginata. Apigenin 7-methyl ether (genkwanin), kaempferol 7-methyl ether (rhamnocitrin) and kaempferol 3,7-dimethyl ether (kumatakenin) constitute the light yellow farina of this species. There may be traces of quercetin 3,7-dimethyl and kaempferol 7,4′-dimethyl ethers, too.

Cheilanthes bullosa. Acecetin is the main flavone of the white excretion, accompanied by small amounts of apigenin and apigenin 7,4′-dimethyl ether.

Cheilanthes grisea. Kaempferol 7,4′-dimethyl ether, kaempferol 3,7,4′-trimethyl ether and apigenin 7,4′-dimethyl ethers are major products; kaempferol 3,7-dimethyl ether, kaempferol and apigenin 7-methyl ethers occur in trace amounts.

Cheilanthes rufa. This species shows the same main flavonoids as *C. albomarginata*, with trace of kaempferol 7,4′-dimethyl ether. *Notholaena candida.* The pure white farina of this fern contains the rare 3,7,3′,4′,5′-pentamethyl ether of myricetin, combretol (proved by UV spectra, too). The second component is likely to be a tetramethyl ether of myricetin.

Notholaena schaffneri. Apigenin and its 7-methyl ether are the sole constituents of the white farina.

Notholaena standleyi. Kaempferol, kaempferol 3- and 4′-methyl ethers as major products are accompanied by the 3,7-, 3,4′- and 7,4′-dimethyl ethers of Kaempferol. This is only the third report of the natural occurrence of combretol (comp. [5]). The other aglycones have been shown recently to occur relatively frequently in lipophilic exudates (see e.g. [6]). It should be noted that the results given here for certain specimens are not necessarily valid for the species in general. Natural variation and even the existence of "chemotypes" with important differences as shown in [7] must be taken into consideration. Results on further species will be published elsewhere [8].

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