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FILICINAE

GYMNOGRAMMACEAE

FLAVONOID FROND EXUDATES FROM TWO JAMAICAN FERNS, *PITYROGRAMMA TARTAREA* AND *P. CALOMELANOS*

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Abstract—Three flavonoids have been identified from the frond exudate of *P. tartarea:* 2′,6′-dihydroxy-4,4′-dimethoxydihydrochalcone, kaempferol 7-methyl ether (rhamnocitrin), and apigenin 7-methyl ether (genkwanin). White-backed fronds of *P. calomelanos* contained 2′,6′-dihydroxy-4′-methoxydihydrochalcone.

AS PART of a biochemical systematic investigation of various fern genera, notably those belonging to *Pityrogramma*, we report here the major exudate flavonoids of *P. tartarea* and *P. calomelanos* from Jamaica, species which are difficult to delimit on morphological grounds. 2′,6′-Dihydroxy-4,4′-dimethoxydihydrochalcone, kaempferol 7-methyl ether (rhamnocitrin) and apigenin 7-methyl ether (genkwanin) were identified in the frond exudate of *P. tartarea* and 2′,6′-dihydroxy-4′-methoxydihydrochalcone in white-backed fronds of *P. calomelanos*. With the exception of kaempferol 7-methyl ether, all the compounds were found to be identical with authentic samples[2] by UV,[3] NMR[3] (of the trimethylsilyl derivatives), m.p. and mixed m.p., and co-chromatography (TLC, polyamide). Kaempferol 7-methyl ether was identified by UV spectral analysis and co-chromatography with an authentic sample.

EXPERIMENTAL

All the fern material was collected by T.J.M. in January, 1970 on St. Andrew's Ridge, Jamaica with the expert assistance of George Procter. All the UV and NMR spectra were determined using standard procedures.[3] M.ps were determined on a Fisher–Johns m.p. block. Because all the flavonoids isolated in the present study are known and were compared directly with authentic samples, we report here only the properties not previously described.

Flavonoids from Pityrogramma tartarea. Ether extracts of frond farina from dried *P. tartarea* material (72·5 g) yielded pinkish yellow crystalline material; the crystals were redissolved in MeOH and the lipophilic material was removed by washing with *n*-hexane. Recrystallization from MeOH yielded crystals of 2′,6′-dihydroxy-4,4′-dimethoxydihydrochalcone, 402 mg, m.p. 143–145°. The NMR spectrum of the trimethylsilyl ether in CCl_4 (ppm, δ) displayed the following signals: two doublets centered at 7·17 and 6·80 (J = 9 c/s) for the 2,6 and 3,5 B-ring protons and a two proton singlet at 6·02 for the 3′ and 5′ A-ring protons; the 4 and 4′ methoxyl moieties gave a 6-proton singlet at 3·78 and a singlet was observed at 2·93 for the four α,β-protons. When the methanolic mother liquor from the above recrystallization step was taken to dryness and the residue thus obtained redissolved in CCl_4, yellow crystals of apigenin 7-methyl ether formed (2 mg), m.p. 282–284°; an additional 4 mg were obtained by column chromatography of the solution over polyamide. The NMR spectral analysis of the trimethylsilyl ether in CCl_4 (ppm, δ): H-2′6′: 7·76 (d), J = 9 c/s; H-3′5′: 6·90 (d), J = 9 c/s; H-6: 6·52 (d), J = 2·5 c/s; H-8: 6·22 (d), J = 2·5 c/s; H-3: 6·37 (s); OCH_3-7: 3·83 (s). A small amount of a third compound (kaempferol 7-methyl ether) was isolated by TLC on polyamide using $CHCl_3$–MeOH–MeCOEt (100:0·6:0·3 v/v).

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Major flavonoid of Pityrogramma calomelanos. Pale silvery plates of 2′,6′-dihydroxy-4′-methoxydihydrochalcone (278 mg), m.p. 175–177°, crystallized from methanol after workup of an ether extract of dried fronds of *P. calomelanos* (30·5 g). NMR spectrum of the trimethylsilyl ether (except for a free 6′-OH) in CCl_4 (ppm, δ); five B-ring protons (H-2,3,4,5,6) appeared at 7·19(s); the two A-ring protons (H-3′,5′) came at 5·97(s); the 4′-methyl group at 3·72(s), the four C-ring protons at 2·92(s), and the 6′-hydroxyl proton at 11·02(s).

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GYMNOSPERMAE

PINACEAE

DITERPENOIDS OF CONES FROM TWO *CEDRUS* SPECIES

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Abstract—Ether extracts from the cones of *Cedrus atlantica* (Endl.) Carr and *C. libani* A. Rich have yielded resin acids of the abietane and pimarane types and related diterpenoids. The extract composition differed from that of the wood for both species but showed characteristic relationships to wood extractives of other species in the Pinaceae.

CHARACTERISTIC wood constituents of species in the family Pinaceae are resin acids of abietane and pimarane types. Thus such acids have been found in the wood of *Abies*,[1–3] *Larix*,[4–6] *Picea*,[7–11] *Pinus*[12] and *Pseudotsuga*.[13] Resin acids have also been found in the bark of Pinaceae species (*Picea*[14] and *Pinus*[15]). The wood and wood oil of different species belonging to the genus *Cedrus* have been studied by various investigators.[16–18] Although

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