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VIOLANTHIN AND ISOVIOLANTHIN FROM THE MARATTIACEOUS FERN *ANGIOPTERIS EVECTA*

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Antiopteris is one of six recognized genera of the Marattiales, a relatively small tropical to subtropical order of ferns. The flavonoids of representatives of this order have been partially characterized by Voirin [1], Swain and Cooper-Driver [2] and Wallace and Story [3], Voirin reported the presence of quercetin with traces of kaempferol in *Marattia excavata*, kaempferol only in *M. fraxinea* (*M. salicinia*), and trace amounts of quercetin as the flavonoid type in *A. evecta*. In contrast to Voirin, Swain and Cooper-Driver [2] identified proanthocyanidins in *Marattia*. Wallace and Story [3] partially characterized two kaempferol *O*-glycosides in *M. salicina*; however, in contrast to previous reports, they only detected *C*- and *O*-glycosides of apigenin in *A. evecta*.

The present endeavour fully characterizes one pair of the mixed di-*C*-glycosylapigenins of *A. evecta* as violanthin (6-*C*-glucosyl-8-*C*-rhamnosylapigenin) and isoviolanthin (6-*C*-rhamnosyl-8-*C*-glucosylapigenin). This is the second documentation of violanthin and the first identification of naturally occurring isoviolanthin.

EXPERIMENTAL

Leaf material (pinnae) of *A. evecta* (G. Forst.) Hoffm. was furnished by Fairchild Tropical Gardens, Miami, Florida, U.S.A. (Accession No. FG-68-156). The material was oven-dried (100°), pulverized in a blender, exhaustively extracted with CH_2Cl_2 and re-extracted with $Me_2CO–H_2O$ (1:1). The latter extract was concd *in vacuo* and taken up in MeOH for chromatography. PC's were each spotted with the extract of 0.8 g of dry plant material, developed in the long direction in TBA [4], rotated 90° and developed in H_2O. The compounds were eluted with $MeOH–H_2O$ (1:1), the solvents removed *in vacuo* and UV spectra determined using standard procedures [4]. The individual compounds of the pair of isomers produced by refluxing each parent compound (2 N HCl, 2 hr) were subsequently reisomerized to form the pair. The above compounds (parent molecules and the pair of isomers produced by acidic refluxing) were co-chromatographed on TLC (cellulose: TBA, 15% HOAc, H_2O, BzAW; Si gel: EPWM). R_f values were determined by 1D PC on Whatman No. 3MM using rutin as an internal standard (R_f rutin: TBA 0.41; 15% HOAc, 0.55; H_2O, 0.21).

Violanthin (*Ae*-1). R_fs TBA, 0.42; 15% HOAc, 0.63; H_2O, 0.32. UV nm: MeOH, 335, 273; MeO^- 398, 332, 283; $AlCl_3$ 383 sh, 351, 305, 279; $AlCl_3$/HCl 382 sh, 346, 294, 279; NaOAc 386, 296 sh, 279. Chromatographic and spectral data are in agreement with a di-*C*-glycosylapigenin or a *C*-diosylapigenin structure [4]. Permethylation of Ae-1 led to one band on Si gel TLC in $CHCl_3–EtOAc–Me_2CO$ (5:4:1) which co-chromatographed with permethyl 6-*C*-glucosyl-8-*C*-rhamnosylapigenin. MS of the compound demonstrated a PM 6-*C*-hexosyl-8-*C*-deoxyhexosylapigenin: M^+ (*m/e* 718), M − 15, M − 31 (100%), M − 47, M − 63, M − 103, M − 133, M − 145 (21%), M − 163, M − 175 (46%), M − 189, M − 205, M − 207, M − 219 (5). Ae-1 co-chromatographed with natural violanthin [6], and syhthetic 6-*C*-glycosyl-8-*C*-rhamnosylapigenin [7] on Si gel TLC (EPWM) and PC in BAW. Acidic refluxing of Ae-1 produced a mixture of Ae-1 and an isomer which was spectrally and co-chromatographically indistinguished from Ae-2 in 5 solvents.

Isoviolanthin (*Ae*-2). R_fs TBA, 0.38; 15% HOAc, 0.41; H_2O, 0.15. UV spectra were identical to Ae-1 and acidic refluxing produced an isomer which was spectrally and co-chromatographically indistinguishable from Ae-1 in 5 solvents. Ae-2 co-chromatographed with synthetic 6-*C*-rhamnosyl-8-*C*-glucosylapigenin [2] on TLC (cellulose: BAW, 15% HOAc; Si gel: EPWM).

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