SULFATED AND NON-SULFATED FLAVONOIDS FROM *PLUCHEA DIOSCORIDIS*

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Pluchea dioscoridis (L.) DC. [syn. *Conyza dioscoridis* (L.) Desf.] (Compositae) (1), yielded four sulfated flavonoids, one of which was characterized for the first time, and four non-sulfated flavonoids. The sulfated flavonols were identified as the 3,7-disulfates of quercetin, isorhamnetin, and kaempferol and the 3-sulfate of isorhamnetin; the four non-sulfated flavonoids are kaempferol 3-rutinoside, quercetin 3-rutinoside, quercetin-3-*O*-β-D-glucoside, and apigenin-6,8-di-*C*-glucoside. *Conyza stricta, Conyza aegyptiaca, Conyza bonatiensis* (2), and *Conyza ivaefolia* (3) contain non-sulfated flavonoids, while *P. dioscoridis* contains the sulfated flavonoids.

Quercetin 3,7-disulfate, previously unreported, gave quercetin and sulfate (confirmed by $BaCl_2$ precipitation) on acid hydrolysis. The linkages of sulfate moieties to the 3 and 7 positions were established from the uv data, λ max (nm) in MeOH, 250, 270 sh, 350; NaOMe, 270, 415 with increase in intensity; NaOAc, 252, 370, 420 sh; $+H_3BO_3$, 259, 380; $AlCl_3$, 275, 330 sh, 430; +HCl, 280, 365 sh, 390. Controlled acid hydrolysis produced two intermediates, quercetin 3-sulfate and quercetin 7-sulfate, as well as quercetin. The identity of the intermediates was confirmed by electrophoretic and uv data. Electrophoretic data of the isolated compounds are in agreement with those reported for disulfates (4-6). The negative fabms showed $[M-H]^-$ at *m/z* 505 ($C_{15}H_8O_{13}S_2Na_2$) indicative of two sulfate moieties with Na^+ counter ions. Moreover, $[M-Na]^-$ was also observed at *m/z* 484.

EXPERIMENTAL

PLANT MATERIAL.—*P. dioscoridis* was collected near the El-Minia University campus in March 1985. The plant material was identified by Prof. M.N. El-Hadidi, Department of Botany, Cairo University. A voucher specimen is deposited in the Department of Botany, El-Minia University.

EXTRACTION, ISOLATION AND IDENTIFICATION OF FLAVONOIDS.—Dried aerial parts of *P. dioscoridis* (200 g) were extracted three times with 30% aqueous MeOH, and the concentrated syrup was chromatographed over a polyamide column eluted with H_2O and then with increasing amounts of MeOH. The H_2O fraction yielded three components of Whatmann 3mm chromatography paper developed for 72 h in *n*-BuOH-HOAc-H_2O (4:1:1). The resulting bands yielded the 3,7-disulfates of quercetin, isorhamnetin, and kaempferol. The 30% MeOH fraction afforded quercetin and kaempferol 3-rutinosides and apigenin-6,8-di-*C*-glucoside, while the 50% MeOH fraction contained quercetin 3-*O*-β-D-glucoside. All compounds were purified over Sephedex LH-20 prior to spectral analysis by uv and ^1H nmr (DMSO-d_6, 60 MHz); the identity of apigenin 6,8-di-*C*-glucoside was confirmed by comparison with an authentic sample (7). The glycosides were hydrolyzed to their respective aglycones and sugars, all of which were identified by authentic sample comparisons.

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