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SHORT COMMUNICATIONS

THE FLAVONOIDS OF *PSIADIA PUNCTULATA*

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ABSTRACT. Fifteen flavonoids were isolated and identified from *Psiadia punctulata* for the first time. They were identified as apigenin, acacetin, chrysoeriol, luteolin, orientin, isoorientin and the 7-glucosides of the three latter, as well as the polymethylated flavonoids cirsilineol, gardenin B, gardenin C, 5-hydroxy-3,6,7,4'-tetramethoxyflavone, 5,3'-dihydroxy-6,7,4',5'-tetramethoxyflavone, and 5-hydroxy-6,7,3',4',5'-pentamethoxyflavone.

INTRODUCTION

Psiadia punctulata (DC.) Vatke (= *P. arabica* Jaub. and Sp.) (Astereae, Compositae) is common to the Arab Peninsula, used by the beduins in casts for broken bones. Tender leaves are dried over an indirect fire and used as casts. From a systematic point of view, *Psiadia* is considered to be one of the genera forming connections between Asian and African flora [1]. Little has been reported on the flavonoids of *Psiadia* species, with only apigenin, aromadendrin and 7-methylaromadendrin being identified in *P. altissima* [2].

RESULTS AND DISCUSSION

The flavonoids of the tribe Astereae are rich in methylated flavones and flavonols. The methylated derivatives are based mainly on kaempferol, quercetin, their 6- or/and 8-hydroxy derivatives as well as the 6- or/and 8-hydroxy derivatives of apigenin and luteolin. A lower number of corresponding 2'-hydroxy derivatives are also reported. Studies reported include species of *Conyza* [3,4,5] and *Psiadia* [2] (subtribe Conyzinae); *Grindelia* [6,7], *Gutierrezia* [8-13], *Haplopappus* [14-16], *Solidago* [17] and *Pteronia* [18] (subtribe Solidagininae); *Aster* [19,20], *Erigeron* [5,21] and *Olearia* [22] (subtribe Asterinae); *Bellis* [21] (subtribe Bellidinae) and *Baccharis* [23-30] (subtribe Baccharinae). C-Glycosylfavones have been reported in the Astereae [31], present in *Haplopappus* [15] and *Hazardia* species [32,33].

Grau [1] pointed out the need to examine in detail the large number of genera belonging to Astereae, without which it is difficult to sort them out into subtribes. This led Herz [34] to state that "in view of the poorly defined subtribes, it should be noted that chemical characters might prove most helpful in future infrageneric classificatory schemes".

As part of a chemosystematic survey of members of the Compositae, we report for the first time the leaf flavonoids of *Psiadia punctulata* (tribe Astereae,

subtribe Conyzinae). They were isolated and identified as apigenin, acacetin, luteolin, chrysoeriol, luteolin 7-glucoside, orientin, orientin 7-glucoside, isoorientin, isoorientin 7-glucoside, cirsilineol (5,4'-dihydroxy-6,7,3'-trimethoxyflavone), gardenin B (5-hydroxy-6,7,8,4'-tetramethoxyflavone), 5-hydroxy-3,6,7,4'-tetramethoxyflavone, 5,3'-dihydroxy-6,7,4',5'-tetramethoxyflavone, 5-hydroxy-6,7,3',4',5'-pentamethoxyflavone (identified tentatively) and gardenin C (5,3'-dihydroxy-6,7,8,4'5'-pentamethoxyflavone). No flavanones were detected in the leaves.

EXPERIMENTAL

Plant material. Psiadia punctulata was collected around El-Tayef, Saudi Arbia. The sample was authenticated by Prof. Dr. A. Fayed, Department of Botany, Faculty of Science, Assiut University. Voucher specimens are deposited at the herbarium of Assiut University.

Isolation and identification of flavonoids. Plant material (leaves and stems) was extracted with EtOH-H_2O (7:3). The concentrated extract was applied on a polyamide column, then eluted with H_2O, followed by increasing concentrations of EtOH. Simple flavonoid glycosides were further purified by preparative PC, while polymethylated flavonoids were separated by preparative TLC. All flavonoids were finally purified on Sephadex LH-20. Common flavonoids were identified through standard methods [34-36], while polymethylated flavonoids were identified by co-chromatography(CC), UV, EIMS and NMR as shown below.

5,4'-Dihydroxy-6,7,3'-trimethoxyflavone (cirsilineol). CC with authentic sample; UV λ_{max} (MeOH) nm: 273, 338; NaOMe, 273, 305sh, 395; $AlCl_3$, 265sh, 278, 305, 370. 405sh, $AlCl_3$-HCl, 260sh, 282, 302sh, 359, 400sh; NaOAc, 270, 345, 405sh, NaOAc-H_3BO_3, 270, 340; MS m/z (rel. int.): 344 [M^+] (95), 343 (32), 329 (52), 326 (12), 181 [A_1-15] (11), 153 [A_1-43] (15).

5-Hydroxy-6,7,8,4'-tetramethoxyflavone (gardenin B). UV λ_{max} (MeOH) nm: 287, 328; NaOMe, 303, 402; $AlCl_3$ & $AlCl_3$-HCl, 287, 310, 354, 405sh; NaOAc & NaOAc-H_3BO_3, 288, 328; MS m/z (rel. int.): 358 [M^+] (62), 343 (100), 211 [A_1-15] (23), 183 [A_1-43] (21); ^{1}H-NMR (270 MHz, acetone d_6): δ 8.08 (d, J = 8 Hz, H-2',6'), 7.17 (d, J = 8 Hz, H-3', 5'), 6.5 (s, H-3), 4.08, 3.99, 3.89, (4 x CH_3O-).

5-Hydroxy-3,6,7,4'-tetramethoxyflavone . CC with authentic sample; UV λ_{max} (MeOH) nm: 275, 338; NaOMe, 290, 310, 380; $AlCl_3$, 260, 287, 367; $AlCl_3$-HCl, 257, 290, 360; NaOAc & NaOAc-H_3BO_3, 275, 338; MS m/z (rel. int.): 358 [M^+] (100), 357 (19), 343 (98), 181 [A_1-15] (21), 153 [A_1-43] (45).

5,3'-Dihydroxy-6,7,4',5'-tetramethoxyflavone . UV λ_{max} (MeOH) nm: 276, 330; NaOMe, 275, 290, 380; $AlCl_3$, 286, 305sh, 358; $AlCl_3$- HCl, 286, 305sh, 353; NaOAc & NaOAc-H_3BO_3, 276, 330; MS m/z (rel. int.): 374 [M^+] (80), 359 (100), 331 (14), 153 [A_1-43] (15); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.18 (d, J = 2.09 Hz, H-6'), 6.95 (d, J = 2.09 Hz, H-2'), 6.59 (s, H-8), 6.55 (s, H-3), 3.99, 3.98, 3.96 (4 x CH_3O-).

5-Hydroxy-6,7,3',4',5'-pentamethoxyflavone(?). UV λ_{max} (MeOH) nm: 278, 330; NaOMe, 298, 335sh, 390; $AlCl_3$, 292, 357; $AlCl_3$-HCl, 294, 350; NaOAc & NaOAc-H_3BO_3, 278, 330; MS m/z (rel. int.): 388 [M^+] (100), 387 (17), 373 (89), 345 (17), 181 [A_1-15] (14), 153 [A_1-43] (33); UV and MS values are in good accordance with literature data [38].

5,3'-Dihydroxy-6,7,8,4',5'-pentamethoxyflavone (gardenin C). UV λ_{max} (MeOH) nm: 283, 328; NaOMe, 270, 311, 390; $AlCl_3$, 290, 312, 358, 400sh; $AlCl_3$-HCl, 290, 312, 353, 410sh; NaOAc & NaOAc-H_3BO_3, 283, 330; MS m/z (rel. int.): 404 [M^+] (71), 389 (100), 211 [A_1-15] (14), 183 [A_1-43] (14); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 102.4 (C-2), 163.4 (C-3), 182.8 (C-4), 149.4 (C-5), 136.5 (C-6), 153.0 (C-7), 132.9 (C-8), 145.7 (C-9), 106.6 (C-10), 126.7 (C-1'), 106.9 (C-2'),

149.6 (C-3'), 138.6 (C-4'), 152.5 (C-5'), 104.8 (C-6'), 61.1 (OMe-6), 62.1 (OMe-7), 61.7 (OMe-8), 56.08 (OMe-4' and OMe-5').

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