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INTERNAL AND EXTERNAL LEAF FLAVONOIDS OF *PERICOME CAUDATA*

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Key Word Index—*Pericome caudata*; Compositae; aerial parts; flavonoids; external and internal accumulation.

Abstract—*Pericome caudata* accumulates four flavonol aglycones externally on leaf and stem surfaces. The glycosides present in the leaf tissue are based on eight further flavonols. This preponderance of tissue flavonoids over exudate flavonoids is unusual.

INTRODUCTION

In our research on occurrence and distribution of flavonoid aglycones in plants, emphasis is on the study of lipophilic plant excretions and their potential chemotaxonomic evaluation [1, 2]. The leaf glycosides may also exhibit different profiles, but the diversity of the external aglycones generally exceeds that of the tissue glycosides. This has been demonstrated recently e.g. for *Ericameria*, *Hazardia*, and *Heterotheca* [3–5]. With *Pericome caudata* we have found a member of the Compositae in which not only the external flavonoid aglycones but also the internal tissue flavonoids are quite interesting.

RESULTS AND DISCUSSION

The leaf and stem exudate of *Pericome caudata*, washed off aerial parts by rinsing with acetone, was worked up by CC as usual. Individual compounds were then identified by direct TLC comparisons with authentic samples and/or by their spectra. The major constituent, 6-hydroxykaempferol 3,6,4′-trimethyl ether, crystallized from the relevent fractions. Further flavonoids observed in the leaf resin are 6-hydroxykaempferol 3,6-dimethyl ether, quercetagetin 3,6,4′-trimethyl ether (centaureidin) and a small amount of kaempferol 3,4′-dimethyl ether (ermanin). In addition we identified two coumarins, namely scoparone and its 7-dimethylallyl ether in the first non-polar fractions eluted from the polyamide column. The latter compound was first described from *Artemisia dracunculoides* [6] and we recently isolated it from *Artemisia glauca* [Wollenweber and Mann, unpublished results].

The methanol extract of the acetone-washed plant material was hydrolysed, partitioned with ethyl acetate, and the epiphase was subject to CC on polyamide. In the hydrolysed tissue-extract we found quercetagetin 6,7,4′-trimethyl ether (eupatin) as the major constituent, along with some quercetagetin 6,7,3′,4′-tetramethyl ether and a trace of quercetagetin 3,6-dimethyl ether (axillarin). Quercetagetin, 6,7,3′,4′-tetramethyl ether is a very rare compound; to our knowledge, it has so far been found only in *Artemisia lanata* [7]. The quercetagetin derivatives were accompanied by quercetin 7,3′-dimethyl ether (rhamnazin), quercetin 7,3′,4′-trimethyl ether, quercetin 3′-methyl ether (isorhamnetin), quercetin (in order of decreasing amount) and a trace of quercetin 7-methyl ether (rhamnetin). These flavonoids are present in the tissue as glycosides.

The flavonoids found to be accumulated on the leaf surface thus are one methyl derivative of kaempferol, two of 6-hydroxykaempferol, four quercetin methyl ethers and three quercetagetin methyl ethers. It is noteworthy that most of the tissue flavonols are 7-methylated, while there is a free 7-OH in the epicuticular flavonols. The aglycones found to be accumulated on the plant surface are clearly different from those on which the leaf glycosides are based. With regard to our earlier observations that in most plants so far studied the variability of the exudate flavonoids generally exceeds that of the tissue flavonoids, the present result with *Pericome caudata* is surprising.

EXPERIMENTAL

Aerial parts of *Pericome caudata* were collected in late August 1985 in the Pinaleno Mountains, Graham Co., Arizona, at an elevation of 2900 m. In this site it is a common dense sub-shrub to 2 m tall that grows with *Artemisia* and *Viguiera* along open roadside on granite substrate. A voucher (G. Yatskievych and M. Windham 85-283A) is kept at ARIZ. Dried aerial parts were rinsed with Me_2CO to dissolve the exudate material. The concd soln was dissolved in boiling MeOH. Fatty and waxy material deposited on cooling and was eliminated by centrifugation. The remainder was dissolved in MeOH and passed down a column of Sephadex LH-20, eluted with MeOH, to separate the flavonoids from the bulk of terpenoids which were not analysed further. The phenolic portion was then fractionated by CC on polyamide, eluted with toluene and increasing quantities of MeCOEt and MeOH. The major flavonoid, 6-hydroxykaempferol 3,6,4′-trimethyl ether, crystallized from the relevant fractions and was characterized by its UV and mass spectra and by its mp. Further flavonoids were identified by direct comparisons with authentic markers on silica gel and on polyamide [8]. The acetone-washed plant material was extracted with 85% and with 50% aqueous MeOH; the combined and concd extracts were hydrolysed by boiling after addition of some HCl. The reaction mixture was, after cooling, partitioned with EtOAc and the epiphase was

further studied in the same manner as the exudate. A minute sample of quercetagetin 6,7,3',4'-tetramethyl was prepared by partial demethylation of artemitin (quercetagetin 3,6,7,3'4'-pentamethyl) with aniline–HCl [9].

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