

Leaf material of *A. thrysoflora* (159.1 g), washed with CH_2Cl_2 , yielded 24 g of nonpolar extract. When this material was passed over a Polyclar AT column eluted with CH_2Cl_2 -MeOH (1:1) with increasing polarity toward MeOH and MeOH- H_2O (1:1), it yielded a mixture of flavones which were separated on a second Polyclar column utilizing toluene-MeOH (8:2) in a gradient to MeOH. The latter column yielded the two major nonpolar flavonoids, the 6-methyl ethers of apigenin and luteolin. The more polar compounds (a diglycoside, a monoglycoside and their aglycone) which occur inside the leaves, were obtained as a mixture after extraction with 80% and 50% aqueous MeOH of the ground CH_2Cl_2 -washed leaf material. The mixture was separated on a cellulose column using 40% HOAc; and the fractions obtained, which were subsequently purified on Polyclar in TBA (*t*-BuOH-HOAc- H_2O , 3:1:1), afforded quercetin, its 3-*O*- β -D-galactoside and 3-*O*- β -D-rhamnogalactoside. All compounds were purified over Sephadex LH-20 in 80% or 100% MeOH prior to analysis by uv, ^1H nmr (as trimethylsilyl ethers), ms, color reactions on paper under uv light, and comparisons with authentic samples. Hydrolysis of the glycosides (0.1 N TFA, 2 h) yielded the expected aglycones and sugar residues.

ACKNOWLEDGMENTS

The work at UT was supported by The National Science Foundation (Grant BSR 8402017) and The Robert A. Welch Foundation (Grant F-130). We also wish to thank Scott Sundberg and Matt Lavin for the collection and identification of *A. solidaginifolia*.

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Received 28 October 1985

FLAVONOID COMPOUNDS FROM *BALLOTA HIRSUTA*

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From the aerial parts of *Ballota hirsuta* Benth. (Labiatae) fourteen flavonoid compounds, six glycosides, and eight aglycones have been isolated and identified. Previously, only 5-hydroxy-7,4'-dimethoxyflavone had been reported from the genus (*Ballota pseudodictamnus*) (1). The aglycones salvigenin (5-hydroxy-6,7,4'-trimethoxyflavone), kumatakenin (5,4'-dihydroxy-3,7-dimethoxyflavone), genkwainin (5,4'-dihydroxy-7-methoxyflavone), ladanein (5,6-dihydroxy-7,4'-dimethoxyflavone), nuchensin (5,6,3'-trihydroxy-7,4'-dimethoxyflavone), isokaempferide (5,7,4'-trihydroxy-3-methoxyflavone), apigenin and luteolin, the flavonoid *O*-glycosides apigenin-7-(*p*-coumaroyl)-glucoside, apigenin-7-glucoside, luteolin-7-glucoside, quercetin-3-glucoside and luteolin-7-rutinoside, and the flavone-C-glucoside vicenin-2 (apigenin-6,8-di-C-glucoside) have been isolated and characterized by uv (2-5) and eims (6-8) and by chromatographic comparisons with authentic compounds.

Within the Labiatae, kumatakenin and isokaempferide have been found previously only in *Salvia glutinosa* (9), nuchensin in *Teucrium nucbense* (10), and quercetin-3-glucoside in *Clethoma bederacea* (11).

B. hirsuta contains 6-hydroxyflavonoids (ladanein and nuchensin) and 6-methoxyflavonoids (salvigenin) that are considered advanced features (12) and constitute the most characteristic chemotaxonomic markers in the Labiatae (13). This last character distinguishes *Ballota* from the taxonomically closely related genus *Phlomis* (14) which lacks 6-substituted compounds (15), although species of both *Phlomis* and *Ballota* contain flavonoid-*p*-coumaroyl-glucosides.

EXPERIMENTAL

PLANT MATERIAL.—*B. hirsuta* aerial parts were collected near Santomera, Murcia, Spain, and a voucher specimen has been deposited in the Herbarium of the Faculty of Sciences of Murcia.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Air-dried and powdered aerial parts of *B. hirsuta* were extracted with *n*-hexane, CHCl₃, and EtOH, successively. The EtOH of the last extract was removed under reduced pressure, and the concentrated extract was resuspended in H₂O and extracted with Et₂O, EtOAc, and *n*-BuOH in succession. The *n*-hexane and CHCl₃ extracts were column chromatographed on silica gel G-100 with solvents of increasing polarity (*n*-hexane, CHCl₃, MeOH), and the Et₂O, EtOAc, and *n*-BuOH extracts were paper chromatographed on Whatman No 3 with solvents, HOAc 30% and *n*-BuOH-HOAc-H₂O (4:1:5, upper phase).

IDENTIFICATION OF THE COMPOUNDS.—Standard uv (2-5) and eims (6-8) methods and chromatographic comparisons against authentic samples (16-18) were employed for the identification of the compounds. After acidic hydrolysis of the glycosidic compounds, the aglycones and sugars were identified by chromatographic comparisons against authentic samples. Apigenin-7-(*p*-coumaroyl)glucoside: eims, permethylated derivative, M⁺ 662 *m/z*. Nuchensin: eims, M⁺ 330 *m/z*. Salvigenin: eims, M⁺ 328 *m/z*. Ladanein: eims, M⁺ 314 *m/z*. Kumatakenin: eims, M⁺ 314 *m/z*. The most common compounds are not described here (luteolin, apigenin, etc.).

Full details on the isolation and identification of the compounds are available from the senior author.

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Received 4 November 1985