

sidifolia (40 g), *S. serrata* (7 g), and *S. soratensis* (20 g) were extracted and the flavonoids isolated using standard procedures (4, 5, 10). All flavonoids were identified by standard spectral (uv, ^1H nmr, ms) and hydrolytic data as well as by authentic sample comparisons and color reaction procedures (4, 5, 7, 9, 10).

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FLAVONOID AGLYCONES AND GLYCOSIDES FROM *TEUCRIUM GNAPHALODES*

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Teucrium species are used in Spanish folk-medicine for their diuretic, antihelminthic, and carminative properties. In addition, these species are difficult to classify, and a chemotaxonomic approach might be useful. For these reasons, we have studied the flavonoids of *Teucrium gnaphalodes* L'Hér (Labiatae), a small plant that is widespread in La Mancha, Spain. Seven aglycones and five flavone glycosides have been isolated and identified.

Previously, several *Teucrium* species were investigated for flavonoids; 5-hydroxy-6,7,3',4'-tetramethoxyflavone and eupatorin were isolated from *Teucrium pseudo-chamaepitys* (1), and diosmin was isolated from *T. gnaphalodes* (2), as the only flavonoid.

From the Et₂O extract, the flavone aglycones cirsimaritin, salvigenin, cirsilineol, cirsilinol, luteolin, apigenin, and a flavanone, naringenin, have been isolated and identified by means of standard uv (3) and ms (4, 5) techniques and chromatographic comparisons against authentic markers. This is the first time that these flavone aglycones have been reported from *Teucrium* species.

From the *n*-BuOH extract, flavone monoglycosides luteolin-7-*O*-β-D-glucoside and apigenin-7-*O*-β-D-glucoside, and flavone diglycosides luteolin-7-*O*-β-D-rutinoside, luteolin-7-*O*-β-D-neohesperidoside (veronicastroside), and luteolin-7-*O*-β-D-sambubioside [xylosyl(1→2)glucoside] have been isolated. Their structures were identified by standard uv procedures, employing the naturally occurring glycosides

and the aglycones obtained upon acidic hydrolysis, ms of their permethylated derivatives (6), and chromatographic comparisons against authentic samples isolated previously in our laboratory from other sources. The sugars were identified after acidic hydrolysis by chromatographic comparisons against xylose, glucose, and rhamnose.

The ms spectra of the permethylated diglycosides allowed the characterization of interglycosidic linkages (6). Thus, the eims of permethylated luteolin-7-*O*- β -D-rutinoside exhibited S+60, S+H, OS, and A+H ions, and permethylated luteolin-7-*O*- β -D-neohesperidoside exhibited S+2H, OS-MeOH, and A+2H ions. Chromatographic separation of these two isomers was rather difficult by tlc and pc techniques, but they were clearly separated by tlc as the permethylated derivatives. The eims of the permethylated luteolin-7-*O*- β -D-sambubioside showed the classical peaks for pentosyl(1 \rightarrow 2)hexosides (6), i.e., OS, OS-MeOH, A+2H, and S-12.

This is the first time that a neohesperidoside and a sambubioside of a flavone have been found in the Labiatae, although flavanone neohesperidosides have been described in this family.

EXPERIMENTAL

PLANT MATERIAL.—*T. gnaphalodes* plants were collected from Pozocañada (Albacete), and a voucher specimen was deposited in the Herbarium of the Faculty of Sciences, University of Murcia (Accession number, 12260).

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Air-dried, powdered, whole plants (50 g) were extracted with EtOH-H₂O (7:3). The EtOH was removed under reduced pressure, and the aqueous concentrate was extracted with Et₂O and *n*-BuOH successively. The aglycones were isolated from the Et₂O extract by cc on silica gel G-100 with CHCl₃ \rightarrow CHCl₃-MeOH (1:1) \rightarrow MeOH and purified by pc on Whatman No. 1 with 30% HOAc and tlc on silica gel with CHCl₃-*n*-hexane-MeOH (40:40:3). The glycosides were isolated from the *n*-BuOH extract by pc on Whatman No. 2 with 30% HOAc and on Whatman No. 1 with *n*-BuOH-HOAc-H₂O (4:1:5, upper phase).

IDENTIFICATION OF THE COMPOUNDS.—Standard uv (3) and ms (5) methods and chromatography (7), including comparisons with authentic samples, were employed for the identification of the compounds. Acid hydrolysis of the glycosides yielded luteolin, apigenin, rhamnose, xylose, and glucose. The sugar sequence and the interglycosidic linkages were established by ms of the permethylated derivatives (6).

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

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