throughout much of the Chihuahuan Desert Region of north-central Mexico and southwestern United States.

The major component of the aqueous methanol-soluble material was a complex mixture of no less than five 6,8-di-*C*-glycosylapigenins: 6,8-di-*C*-glucosylapigenin (vicenin-2) (**1**), 6-*C*-xylosyl 8-*C*-glycosylapigenin (vicenin-1) (**2**), 6-*C*-arabinopyranosyl 8-*C*-glucosylapigenin (isoschaftoside) (**3**), 6-*C*-glucosyl 8-*C*-arabinopyranosylapigenin (schaftoside) (**4**) and 6-*C*-glucosyl 8-*C*-arabinosylapigenin (neoschaftoside) (**5**). **1**, **3** and **4** were isolated in crystalline form and unambiguously identified by IR, MS and co-chromatography. To our knowledge, this is the first identification of isoschaftoside as a natural compound. Previously, it had been obtained by acid treatment of natural schaftoside [2]. Compound (**2**) was found as a by-product in the mother liquors of (**3**). Its presence was detected by TLC of the permethylation product of these mother liquors, PM (**2**) and PM (**3**) being well separated. The MS of PM (**2**) was identical with that of PM (vicenin-1). Then TLC of the mother liquors on activated silicagel in APEM P 20 allowed the confirmation of (**2**).

Compound (**5**) previously isolated from *Catananche caerulea* [3] and then misnamed isoschaftoside, is an isomer of schaftoside in which arabinose could be in the furanose form. Heating schaftoside with acids led to a mixture of (**3**), (**4**), and (**5**). (**5**) appeared as the faster migrating band on PC in BAW. Elution of this band gave a single spot (in BAW) with the same R_f as (**5**). TLC of the permethylation product of the eluate indicated the presence of three bands, all giving MS characteristic for PM 6-*C*-hexosyl 8-*C*-pentosylapigenins, one of these bands co-chromatographing with PM (**5**).

The $CHCl_3$ extraction yielded four flavonoid methyl ethers: 3-*O*-methylquercetin, 3, 7-di-*O*-methylkaempferol, 5,4′-dihydroxy-6,7dimethoxyflavone (cirsimaritin) and 5,7,4′-trihydroxy-6-methoxyflavone (hispidulin). These were isolated and identified by UV, NMR and TLC comparison with authentic samples. Spectral values and color reactions for these compounds were identical with previously reported values [1,4,5].

EXPERIMENTAL

Leaf material was collected near Alpine, Texas (Brewster Co.) and a voucher specimen is deposited in the University of Texas at Austin, Texas (*Bacon* and *Hartman* 1443). All 2-D chromatograms were on Whatman 3MM paper and were developed first in TBA (*t*-BuOH–HOAc–H_2O, 3:1:1) and then in 15% HOAc. NMR spectra were recorded using tetramethylsilane as an internal standard. Preparation of TMS ethers, permethylation products and TLC were carried out by standard procedures [5,6]. Air-dried and powdered leaves (150 g) of *Flourensia cernua* were extracted exhaustively with $CHCl_3$. Combined extracts were taken to dryness *in vacuo*, yielding a dark green syrup (10.5 g). This syrup was chromatographed over polyamide (200 g packed in elution solvent); the column was initially washed with $CHCl_3$–EtOAc (3:1) and later $CHCl_3$–MeOH–MeEtKetone (12:3:1). Bands were collected in fractions, and purified by TLC in appropriate solvents. The four methylated flavonoids were identified from the $CHCl_3$-soluble material. After drying to remove residual $CHCl_3$, the leaf material was re-extracted with aq 85% MeOH. The extract was taken to dryness *in vacuo*, yielding a dark brown syrup (5 g). This was taken up in H_2O and partitioned with $CHCl_3$. The aq portion was again taken to dryness and chromatographed over polyamide (200 g packed in 90% MeOH), eluting with progressively more aq MeOH. Bands were collected as fractions and purified by rechromatographing over polyamide (50 g packed in 100% MeOH). One band from the column yielded compounds **1**–**5** as a mixture of di-*C*-glycosylapigenins (from UV and R_f). MS of the permethylated mixture showed it to contain di-*C*-hexosyl and *C*-pentosyl *C*-hexosyl apigenins in the ratio (1:3). Cellulose column chromatography of the mixture in 15% HOAc directly gave crystalline (**3**) from the last fractions, (**2**) being present in the mother liquors. The first fractions contained a mixture of (**1**), (**4**) and (**5**) which were separated by repeated PC in BAW (4:1:5).

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A NEW FLAVONOID FROM *PLUCHEA SAGITTALIS**

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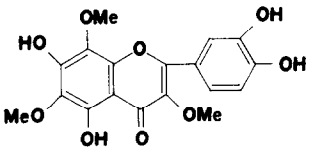
Key Word Index—*Pluchea sagittalis*; Compositae; 5,7,3′,4′-tetrahydroxy-3,6,8-trimethoxyflavone.

Plant. Pluchea sagittalis (Lam.) Cabrera (Compositae) is a perennial shrub that grows in Northeastern Argentina (local name "lucera" or "yerba del lucero") [1]. *Source.* Aerial parts were collected at Concepción del Uruguay, Province of Entre Ríos, Argentina. A voucher specimen is deposited in the University Herbarium (Museo de Botánica, Universidad de Buenos Aires,

* Part 10 in the series "Flavonoids from Argentine Medicinal Plants". For Part 9 see (1975) *planta Méd.* **27**, 226.

entina). *Uses.* It has been reported to have medicinal perties [2,3]. *Previous work.* Phytochemical screening]. Essential oil [7–9]. Pharmacological activity [10]. *resent work.* From the $CHCl_3$ extract we have iso- d a new flavone, whose structure has been determined , [11], IR, NMR, MS and methylation product) as ',4'-tetrahydroxy-3,6,8-trimethoxyflavone (**1**). This is first report of this compound as a natural product.



(1)

EXPERIMENTAL

ir dried, ground material (600 g) was extracted 24 hr at n temp. with 3 × 5.5 l 25% aq MeOH. The aqueous OH extracts were evaporated to dryness, taken into hot) and partitioned with petrol and $CHCl_3$. The petrol act contained no flavonoids and was discarded. The Cl_3 extract was evaporated to dryness and applied to a mn packed with Sephadex LH_{20} and eluted with C_6H_6, Cl_3 and MeOH. The MeOH eluates were concentrated applied as bands on cellulose TLC and developed with HOAc. The lowermost band was scrapped from the plate, ed with MeOH and taken to dryness. This band afforded ',4'-tetrahydroxy 3,6,8-trimethoxyflavone which crystal- l from ETOH as yellow crystals mp 167–169°. ',4'-Tetrahydroxy-3,6,8-trimethoxyflavone; (a) purple (UV) ellow–brown (UV/NH_3); R_fs: TBA 0.96, HOAc 15% 0.41; λ_{max} (nm): MeOH, 260, 275 *sh*, 345; NaOMe, 270, 282 85; $AlCl_3$, 277, 305 *sh*, 365 *sh*, 435; $AlCl_3$–HCl, 265, 282, *sh*, 365; NaOAc, 270, 380; NaOAc–H_3BO_3, 265, 367. R (60 MHz), (DMSO-d_6) using TMS as internal standard, als at δ 7.60 (2H, *d*, *J* 16 Hz), δ 6.85 (1H, *d*, *J* 8 Hz), 97, 3.85, 3.80 (9H, 3 OMe). MS, principal peaks in *m/e* (100%) (M^+), 361 (100%) ($M^+ - 15$), 344 (50%), 331 (10%), (10%), 301 (7%), 180 (10%), 153 (10%), 137 (25%), 121 %).

The MS spectrum of the compound showed a parent peak at *m/e* 376 ($C_{18}H_{16}O_9$ required 376) with a base peak at *m/e* 361 (M − 15) diagnostic for 3,6,8 methoxylated flavones [12,13]. Methylation with CH_2N_2 afforded 5,6,7,8,3,3',4'-heptamethoxyflavone; pale yellow prisms from Et_2O–petrol mp 131–132° (lit. 130–131°) UV λ_{max} (nm) 340, 255 [14]. No shifts with NaOMe, $AlCl_3$, $AlCl_3$–HCl, NaOAc and NaOAc–H_3BO_3; NMR corresponding to this heptamethoxyflavone.

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FLAVONOL GLYCOSIDES OF *NERISYRENIA* (CRUCIFERAE)

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our chemosystematic survey of the genus *Nerisyrenia* ded several flavonol glycosides including the pre- usly reported quercetin, kaempferol and isorhamnetin -neohesperidosides [1]. We report here the isolation l identification of four additional flavonol glycosides, 3-*O*-glucoside 7-*O*-gentiobiosides of kaempferol (**1**), isohamnetin (**2**) and quercetin (**3**) along with quercetin 3-*O*-neohesperidoside 7-*O*-glucoside (**4**).

Acid hydrolysis of each compound afforded the respective aglycone (i.e. kaempferol from **1**, isorhamnetin from **2** and quercetin from **3** and **4**) as determined by PC co-chromatography with authentic aglycone samples and