Die Substanzen III–VIII wurden mit Hilfe von Hydrolysen, UV, NMR (vgl. Tab. 1) und z.T. Cochromatographie mit authentischen Substanzen als Rutin (III), Isoquercitrin (IV), Isorhamnetin-3-*O*-rutinosid (V), Isorhamnetin-3-*O*-glucosid (VI), Albosid [4] (VII) und Isorhamnetin (VIII) identifiziert. Die Hauptmenge machten V und VI aus.

Vom biogenetischen Standpunkt bilden die Substanzen III–VII eine interessante Reihe, bestehend aus den Glucosiden und Rhamnoglucosiden von Quercetin (IV, III) und dessen Mono- (VI, V) und Dimethyläther (VII); nur das Rutinosid des Dimethyläthers konnte nicht nachgewiesen werden.

Durch Cochromatographie der isolierten blau fluoreszierenden Verbindungen mit authentischen Substanzen und UV wurden Chlorogen-, Isochlorogen-, Ferula- und Gentisinsäure, sowie Äsculetin und Äsculin identifiziert. Aus Aceton-Extrakten wurden die folgenden Substanzen isoliert und durch Cochromatographic identifiziert: Catechin, Epicatechin (Hauptsubstanzen), die Proanthocyanidine B2, B4, neben wenig B1 und B3 (Struktur, siehe Lit. [5]). Dadurch unterscheidet sich *S. alba* von *S. caprea* und *S. viminalis*, die als Hauptsubstanzen die Proanthocyanidine B3 und C2 enthalten [5].

EXPERIMENTELLES

Das Pflanzenmaterial, das in der Nähe von Gmünd geerntet wurde, wurde von Dr. R. Müller, Weleda, auf seine Identität überprüft. Belegexemplare befinden sich bei uns. Die NMR-Spektren wurden von den TMSi-Derivaten in CCl_4 auf einen Jeol JNM-C-60 HL Instrument (VI, VII) oder einen Bruker HFX 90 Gerät (I–III, V) mit TMS als innerem Standard aufgenommen. R_f-Werte wurden durch DC auf Cellulose mit $CHCl_3$–HOAc–H_2O (55:45:10) als Fließmittel bestimmt.

Isolierung der Flavonoide. Die frischen Blätter (22 kg) wurden mit MeOH kalt extrahiert. Die eingedampften Extrakte wurden nach Aufnehmen in heißem H_2O durch Extraktion mit versch. Lsg.-Mittel in 4 Frakt. aufgeteilt. Diese Frakt. wurden durch präparative PC (HOAc 15%) in 14 Zonen aufgeteilt. Diese Zonen wurden nach Elution mit MeOH chromatographiert an Sephadex LH-20 (70% MeOH), wodurch u.a. I und II als reine Stoffe gewonnen werden konnten.

Terniflorin (I), Schmp. 267° (MeOH) (Lit. [3] 266–7° (Zers.)). R_f 0,49. UV (MeOH), λ_{max} nm: 269, 319; (NaOMe): 272, 305, 367; (MeOH–$AlCl_3$): 276, 301, 321, 381; ($AlCl_3$–HCl): 278, 300, 322, 375; (NaOAc): 268, 325, 383; (NaOAc–H_3BO_3): 269, 321. IR (KBr), ν_{max} cm^{-1}: 1690 (O=C–(C=C)–OR) (Lit. [3] 1686).

Apigenin-7-O-(4-O-p-cumarylglucosid) (II). Schmp. 239–42° (MeOH). R_f 0,63. UV (MeOH), λ_{max} nm: 268, 333; (NaOMe): 275, 327, 391; (MeOH–$AlCl_3$): 276, 303, 348, 384; ($AlCl_3$–HCl): 277, 301, 343, 382; (NaOAc): 276, 385; (NaOAc–H_3BO_3): 269, 344. IR (KBr), ν_{max} cm^{-1}: 1690 (O=C–(C=C)–OR).

3',7-Dimethylquercetin-3-O-glucosid (*Albosid*) (VII). Schmp. 179–82° (MeOH) (Lit. [4] 178–80°). R_f 0,75.

Hydrolyse von I. 2 mg I wurden bei 100° mit 3 ml 1 N HCl (H_2O–MeOH (1:1)) 20 min. hydrolysiert.

Methanolyse von I. 5 mg I wurden bei Raumtemp. mit 4 ml 0,2% NaOMe–MeOH versetzt. Proben wurden stündlich entnommen und DC untersucht.

Umbildung von II in I. 2 mg II wurden in 2 ml MeOH gelöst und bei Raumtemp. 4 Wochen stehengelassen. Zunächst täglich, dann wöchentlich wurden Proben entnommen und DC untersucht (nach 4 Wochen 50%ige Umbildung).

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NEW FLAVONOIDS FROM *FLOURENSIA CERNUA*

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Key Word Index—*Flourensia cernua*; Asteraceae; 6,8-di-*C*-glycosylflavones; 3-*O*-methylquercetin; 3,7-di-*O*-methylkaempferol.

In connection with a biosystematic investigation of the genus *Flourensia*, five 6,8-di-*C*-glycosylflavones and two methoxylated flavonols have been isolated and identified from leaf material of *Flourensia cernua* DC. In addition, two previously reported [1] methoxylated flavones, cirsimaritin and hispidulin were also characterized. *Flourensia cernua* (commonly called tarbrush, black brush or ojasen) is a frequent member of the desert vegetation

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,

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