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6,8-DI-*C*-GLUCOSYLFLAVONES FROM *LARREA TRIDENTATA* (ZYGOPHYLLACEAE)

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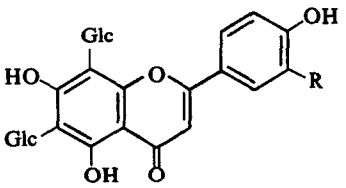
Key Word Index—*Larrea tridentata*; *L. divaricata*; Zygophyllaceae; 6,8-di-*C*-glucosylapigenin; 6,8-di-*C*-glucosylchrysoeriol; scoparin; glycoflavones.

We previously described 19 flavonoid aglycones from *Larrea tridentata* and *L. divaricata* [1–3]. In continuation of our investigations of *L. tridentata*, we now report the isolation and characterization of two *C*-glucosyl-flavones, 6,8-di-*C*-glucopyranosylapigenin (vicenin-2) (**1**) and a new flavonoid from nature [4], 6,8-di-*C*-β-D-glucopyranosylchrysoeriol (**2**).

Compound **1** was isolated as pale yellow crystals (from MeOH), mp above 238° (dec); λ_{max} (MeOH): 274, 302, 330 nm. All the standard [5] UV data and R_f values as well as the NMR spectrum of the trimethylsilyl ether of **1** were in accord with an apigenin 6,8-di-*C*-hexoside. It was therefore directly compared with an authentic sample of 6,8-di-*C*-β-D-glucopyranosylapigenin [6] by IR and co-chromatography and shown to be identical with it.



1 R = H
2 R = OMe

Compound **2** was isolated as yellow pellets (from MeOH), mp 110–150° (gradual dec); λ_{max} (MeOH): 273, 347 nm. All the standard [5] UV data and R_f values supported a chrysoeriol 6,8-di-*C*-hexoside structure. Furthermore, the MS of the PDM derivative showed the expected M^+ at *m/e* 811 and a fragmentation pattern for a undecadeuterio 6,8-di-*C*-hexosylchrysoeriol [7]. An authentic sample of 6,8-di-*C*-β-D-glucopyranosylchrysoeriol was prepared by *C*-glucosylation of scoparin [8] and the synthetic material was shown to be identical with compound **2** by IR and co-chromatography and by co-chromatography of their PM derivatives.

EXPERIMENTAL

Mps were uncorr. UV spectra were carried out by standard procedures [5]. The NMR spectrum of the TMS ether of **1** was measured at 60 MHz in CCl_4 with tetramethylsilane as an internal standard. Air-dried and ground leaf material (500 g) from a diploid population of *L. tridentata* (collected near Alpine, Texas, July, 1973) was extracted with 85% aq. MeOH; the extract was filtered and the filtrate was concd to an aq. suspension: the latter was extracted with ether repeatedly until the ether layer was colorless. The aq. layer was taken to dryness *in vacuo*. The residue was dissolved in MeOH and the soln filtered. More than 200 PCs of the MeOH solution were run with TBA. The bands with R_f values of from 0.05 to 0.30 were eluted with MeOH. From the concd extract 100 PCs were run with 15% HOAc; the bands with R_f values from 0.35 to 0.50 and from 0.50 to 0.60 were extracted separately with MeOH. Both extracts were evaporated and two residues were each chromatographed through a polyamide column using MeOH for elution. Recrystallization from MeOH of the column-chromatographed material (originally from bands of 0.35 to 0.50 R_f values on paper) gave pale yellow crystals of 6,8-di-*C*-glucosylapigenin (**1**): bands from paper of R_f values between 0.50 and 0.60 gave

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(after column chromatography) yellow pellets of 6,8-di-C-glucosylchrysoeriol (2). R_f values for 1 on Whatman 3MM: 0.87 (TBA), 0.60 (15% HOAc); on TLC cellulose: 0.47 (15% HOAc), 0.47 (*n*-BuOH–27% HOAc, 1:1); on TLC Si gel: 0.48 (EtOAc–Py–H_2O–MeOH, 16:3:2:1). R_f values for 2 on Whatman 3MM: 0.14 (TBA), 0.47 (15% HOAc); on TLC cellulose: 0.46 (15% HOAc), 0.20 (*n*-BuOH–27% HOAc, 1:1); on TLC Si gel: 0.43 (EtOAc–Me_2CO, 5:4). No differences were observed in any of the R_f values between the natural and synthetic products. MS of the PDM derivative of 2: *m/e* (%), M^+ 811 (11); M-18, 793 (15); M-34, 777 (100); M-109, 702 (5); M-173, 638 (12); M-184, 627 (43).

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3,6,3′,5′-TETRAMETHOXY-5,7,4′-TRIHYDROXYFLAVONE FROM *TILLANDSIA USNEOIDES*

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Key Word Index—*Tillandsia usneoides*; Bromeliaceae; 3,6,3′,5′-tetramethoxy-5,7,4′-trihydroxyflavone.

We report the isolation and structural determination of a new 6-methoxylated myricetin derivative 1, 3,6,3′,5′-tetramethoxy-5,7,4′-trihydroxyflavone, from leaves and stems of *Tillandsia usneoides*. The mass spectrum of the compound exhibited a molecular ion at *m/e* 390 for $C_{19}H_{18}O_9$ in agreement with a flavone containing four methoxyl and three hydroxyl substituents; these substituents were confirmed by the NMR spectrum of the trimethylsilyl ether of I in CCl_4: signals were observed for two protons at δ7.26 in accord with protons at 2′ and 6′ and one at δ6.48 suggesting either a 3, 6 or 8 proton [2], and for four methoxyl groups (two at 3.85 and one each at 3.8 and 3.7). The structural question remaining was to determine the positions of the methoxyl and hydroxyl groups. Since the compound exhibited a band I at 359 nm in MeOH typical of a flavonol and since it appeared as a purple spot on paper under UV light, a hydroxyl group was assigned to the C-5 position and a methoxyl to C-3 [2].

The UV spectrum in $AlCl_3$–HCl confirmed the presence of a hydroxyl group at C-5 and also indicated that oxygenation was present at C-6 (band I at 377 relative to the MeOH spectrum band I at 359 [3]. The presence of a C-4′ hydroxyl group was indicated by the change in color to yellow–green when the spot on paper was fumed with ammonia; this assignment was confirmed by a bathochromic shift of 68 nm and an increase in intensity of band I for the NaOMe UV spectrum relative to band I in the MeOH spectrum [2]. The presence of a low intensity band in the NaOMe spectrum at 340 nm is typical for flavonols with a C-7 hydroxyl group [1]. This latter assignment is supported by a bathochromic shift of 18 nm of band II in the NaOAc spectrum (270 nm) relative to Band II in the MeOH spectrum (252 nm) [2].

The NMR spectrum in CCl_4 exhibited a singlet integrating for 6 protons at 3.85δ and two singlets integrating for 3 protons each at 3.8 and 3.7. This indicated four methoxyl substituents, two of which were equivalent [2]. Since it was known from the UV spectra and color on paper that the C-5, C-7, and C-4′ positions had free hydroxyl substituents, the two singlets integrating for 3 protons each were assigned to the C-3 and C-6 positions [2]. The singlet integrating for 6 protons was assigned to two equivalent methoxyl groups at the C-3′ and C-5′. The spectral analyses establish that the new flavonol is 3,6,3′,5′-tetramethoxy-5,7,4′-trihydroxyflavone.

EXPERIMENTAL

A voucher specimen (D. S. Lewis 2) is deposited in the University of Texas Herbarium. Fresh, ground leaves and stems of *Tillandsia usneoides* (collected in Travis Co., Texas, June 6, 1974) were extracted at room temperature 2 × CH_2Cl_2 for 24 hr. The extract was filtered and concentrated *in vacuo*. The concentrate was chromatographed over polyamide packed in $CHCl_3$–EtOAc (7:3). The seventh fraction, appearing as a yellow band on the column, was taken to dryness and washed repeatedly with spectral grade MeOH. When the MeOH washings were taken to dryness yellow crystals of 1 were obtained. R_f values: 0.8 (TBA), 0.15 (15% HOAc); UV:MeOH −252, 272, 359; NaOMe: 266, 340, 427 (no decomposition); $AlCl_3$: 268, 274sh,