(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, 312, 400; $AlCl_3/HCl$: 262, 280, 310, 377, 412sh; NaOAc: 270, 320, 418; $NaOAc/H_3BO_3$: 275, 365. NMR: C_6D_6: 3.76 and 3.66 (OMe groups at 3 and 6); 3.52 (OMe groups at 3′,5′); 7.45 (H-2′, H-6′); 6.7 (H-8); data for CCl_4 given in text. MS (values in parenthesis represent relative intensities): M^+ 390 (100); $M + H^+$ 391 (51); $M - H^+$ 389 (44); 376 (35); $M - Me^+$ 375 (81); 372 (28), 357 (26), 347 (50), 329 (32), 181 (24), 165 (20).

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PHENOLIC GLYCOSIDES FROM *SOLANUM GLAUCOPHYLLUM*: A NEW QUERCETIN TRIGLYCOSIDE CONTAINING D-APIOSE

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Key Word Index—*Solanum glaucophyllum*; Solanaceae; phenolic and flavonoid glycosides.

Abstract—Eight phenolic glycosides have been isolated from the leaves of *S. glaucophyllum*, one of them being quercetin-3-*O*-(2^G-β-D-apiosylrutinoside).

INTRODUCTION

It has been established that cattle feeding on leaves of *S. glaucophyllum* Desf. (*S. malacoxylon* Sendt.) [1] contract a disease named 'enteque seco' in Argentine and 'espichamiento' in Brazil [2]. The active principle has been isolated and tentatively characterized as a complex glycoside of 1,25-dihydroxy-vitamin D_3 [3]. We now report on the phenolic constituents in the leaves of the plant.

RESULTS

The fraction extracted by butanol, from an initial water extract from the leaves, yielded hydroquinone, kaempferol and quercetin and the following known glycosides: arbutin, *O*-methylarbutin, isoquercitrin, avicularin, rutin, kaempferol-3-*O*-rutinoside and isorhamnetin-3-*O*-rutinoside. A new amorphous quercetin trioside was isolated and identified as quercetin 3-*O*-(2^G-β-D-apiosylrutinoside). It is a new example of a flavonoid trioside which has a monosaccharide linked to carbon 2 of the D-glucose moiety of rutinose [4]. This compound 1, on mild hydrolysis produced D-apiose and rutin. Methylation with diazomethane in methanol–ether and subsequent hydrolysis with 2N HCl, afforded 5,7,3′,4′-tetra-*O*-methylquercetin. Hydrolysis of the permethylated glycoside gave permethylated L-rhamnose and 3,4-di-*O*-methyl-D-glucose showing that the apiose residue was attached at carbon 2 of glucose. Preparation of the 1,2:3,5-di-*O*-isopropylidene derivative showed that the apiose belonged to the D-series. By applying Klyne's rule to the new glycoside as used by Hulyalkar *et al.* [5] in the case of apiin, it is clear that the apiose must be linked as the β anomer. The difference between the molecular rotation of apiin (−754°) and 7-*O*-(D-glucopyranosyl)-apigenin (−349°) was −405°. In our case, the molecular rotations in methanol of the triglycoside (−461°) and rutin (+10°) gave a difference value very close to that reported by the above authors.

EXPERIMENTAL

Mps are uncorr. All known compounds were obtained in crystalline condition and identified by mp, mmp, $[\alpha]_D$. UV