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6-METHOXYKAEMPFEROL 3-*O*-GLUCOSIDE FROM *FLAVERIA BROWNII*

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We report the isolation and structure determination of a new flavonol glycoside, the 3-*O*-glucoside of 6-methoxykaempferol, from the leaves and stems of *Flaveria brownii* collected in south Texas.

The mass spectrum of the perdeuteriomethyl ether of the glycoside gave an aglycone ion at *m/e* 367 (97% relative intensity to the base peak) as expected for the loss of the C_3-*O*-glycosyl moiety and the introduction of three deuteriomethyl groups at the 5,7 and 4′ positions on a 6-methoxykaempferol skeleton. Other prominent peaks were *m/e* 368 (40%), 366 (10%) and 352 (60%); this latter peak is typical for 6-methoxyflavonols. The sugar obtained by 2N HCl hydrolysis of the natural product was identified as glucose by co-chromatography on PC and by GLC of its trimethylsilyl ether. The aglucone appeared yellow-green when viewed on paper over UV light, typical for a flavonol. Moreover, the aglycone was identical with an authentic sample of 6-methoxykaempferol [1] by co-chromatography in three different systems.

The NMR spectrum (in CCl_4) of the trimethysilyl ether of the natural product gave typical kaempferol B-ring proton signals: two doublets (J = 9Hz) at δ 7.9 for H-2′ and H-6′ and at δ 6.86 for H-3′ and H-5′. Other aromatic signals included a singlet at δ 6.45 typical for an isolated proton at C-8, and a sharp three-proton methoxy singlet at δ 3.65. The latter signal shifted upfield only 0.07 ppm in benzene in accord with a 6-methoxyl group. A one-proton doublet (J = 5Hz) at δ 5.8 could be assigned to the H-1 proton in a C_3-*O*-glucosyl moiety; six other glucosyl protons appeared between 3.3 and 3.58 ppm. The UV spectrum of the natural product in MeOH exhibited Band I at 338 nm and this combined with the absence of a shoulder on Band II supported a kaempferol-type B-ring. The Band I shift of 64 nm with an increase in intensity for the NaOMe spectrum is in accord with a 4′-hydroxyl group. The 24 and 21 nm shifts of Band I in $AlCl_3$ and $AlCl_3$/HCl, respectively (both relative to Band I in MeOH) are in the range for a 6-methoxyl group in a C_5-OH, C_3-*O*-substituted flavonol [2]. The shoulder at 398 nm on Band I in $AlCl_3$/HCl is also in accord with the presence of a 6-methoxyl group [2]. The presence of Band III in the NaOMe spectrum at 330 nm and Band I in NaOAc appearing at shorter wavelength relative to Band I in NaOMe are diagnostic for a free 7-hydroxyl group [3]. Since the aglucone is 6-methoxykaempferol, the above data establish a 3-*O*-glucosyl group; thus, the natural product is 6-methoxykaempferol 3-*O*-glucoside, a new compound from nature.

EXPERIMENTAL

Air dried leaves and stems of *Flaveria brownii* (collected at Port Aransas, Texas; a voucher specimen, Powell 2802, is deposited in LL Herbarium, The University of Texas at Austin) were ground to a fine powder, which was extracted at room temp. with a 85% aq. MeOH for 24 hr. The extract was filtered and concd *in vacuo*, then extracted with $CHCl_3$ followed by EtOAc. The EtOAc fraction was chromatographed over polyamide packed in MeOH; 6-methoxykaempferol 3-*O*-glucoside was eluted with MeOH in the first fractions: R_f values 0.66 (TBA); 0.54 (15% HOAC); UV: λ_{max}^{MeOH} 271, 293, 338 nm; NaOMe: 281, 330, 402 (no dec.) nm; $AlCl_3$: 278, 301 *sh*, 362, 392 *sh*; $AlCl_3$/HCl: 281, 307 *sh*, 359, 398 *sh*; NaOAc: 273, 312 *sh*, 336, 396; NaOAc/H_3BO_3: 270, 346. Acid hydrolysis of the glycoside afforded glucose and 6-methoxykaempferol. The aglycone was identical with an authentic sample by polyamide TLC, $CHCl_3$–MeOH–MeCOEt–Me_2CO (10:10:5:1) R_f 0.72; PC, TBA and 50% HOAc, R_f 0.80 and 0.62, respectively.

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