Diosmin-peracetate. Mp 129–130°, lit. 129–130° [1]; (MW calc. for $C_{44}H_{48}O_{23}$ (MS): 944.2687. Found: 944.2577). ^1H NMR (90 MHz, PFT, $CDCl_3$) [ppm]: δ 7.74 (*dd*, $J = 9$ and 2.2 Hz, 1H at C-6′); 7.56 (*d*, $J = 2.2$ Hz, 1H at C-2′); 7.09 (*d*, $J = 9$ Hz, 1H at C-5′); 6.73 (*d*, $J = 2.1$ Hz, 1H at C-8); 6.64 (*d*, $J = 2.1$ Hz, 1H at C-6); 6.51 (*s*, 1H at C-3); 5.33–4.87 (*m*, 7H of sugar); 4.71 (*d*, $J = 0.6$ Hz, 1H of C-1 of rhamnose); 3.91 (*s*, 3H of OMe group); 4.36–3.60 (*m*, 4H of sugar); 2.43, 2.37, 2.10, 2.08, 2.07, 2.06, 2.05, 2.04, 1.92 (*s*, 27H of 9 Me-acetate), 1.14 (*d*, $J = 6$ Hz, 3H of Me-rhamnose).

Tamarixetin 7-O-*rutinoside* **4**. 120 mg peracetylated tamarixetin 7-*O*-rutinoside were dissolved in 25 ml dry MeOH and 0.5 ml 5% NaOMe were added. The soln was heated at 65° for 10 min and evapd to dryness. It was then dissolved in 50 ml H_2O and extracted with 25 ml *n*-BuOH (×3). The *n*-BuOH was removed *in vacuo* and the substance obtained was subjected to column chromatography on a 2 g Si gel column for purification: crystals, mp 293–295°. IR (KBr) cm^{-1}; 3600–3200, 2945, 1650, 1620, 1580, 1480, 1320, 1175, 1145, 1125, 1090, 1060, 1040.

Hydrolysis of tamarixetin 7-O-*rutinoside*. 50 mg **4** were dissolved in 20 ml 2 N H_2SO_4 and the soln was refluxed for 6 hr at 165°. After cooling, the reaction mixture was diluted with 100 ml H_2O and extracted with 25 ml (×4) of *n*-BuOH. (a) The *n*-BuOH layer was washed with H_2O and evapd to dryness: mp 255–258° (lit. [5] 259–260°). (MW calc. for $C_{16}H_{12}O_7$ (MS): 316.058. Found: 316.055). MS *m/e*: 316 (M^+, 100%); 301 (M − Me, 56.7); 287 (M − CHO, 5); 273 M − C_2H_3O, 15.7); 151 (M − $C_8H_5O_4$, 21); 149 (M − $C_8H_7O_4$, 17); 83; 71; 69. The H_2O layer was neutralized with $BaCO_3$ and evapd. In this way 15 mg mixture of sugars were obtained. These were identified by means of PC and TLC as L-rhamnose and D-glucose. Quantitative sugar analyses were also carried out [13].

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A NEW FLAVONE FROM *GOMPHRENA MARTIANA*

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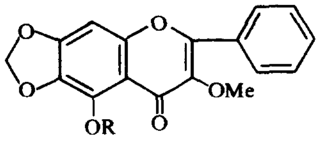
Key Word Index—*Gomphrena martiana*; Amarantaceae; flavonoid; 3,5-dimethoxy-6,7-methylenedioxyflavone.

Little is known of the chemical constituents of the genus *Gomphrena*. Isolation of betacyanins from *G. globosa* L. is the only previous work reported in the literature [1]. Present examination of *G. martiana* led to the isolation of a flavone that was characterized as 3,5-dimethoxy-6,7-methylenedioxy flavone (**1**) by means of spectroscopic and chemical procedures. This compound has been previously synthesized [2] but there are no reports on its isolation from natural sources.



1 R = Me
2 R = H

RESULTS AND DISCUSSION

From the petrol extract of whole plants a precipitate separated on concentration. On repeated crystallizations from EtOH it yielded white needles, mp 198–200°. The compound was not phenolic, as shown by a negative $FeCl_3$ reaction, but it gave positive Labat reaction indicating the presence of a methylenedioxy group [3]. The UV and a positive Shinoda test [4] were consistent with a flavone structure. The ^1H NMR signals of the aromatic protons at δ 8 (2H, *m*, H-2′ and H-6′) and 7.43 (3H, *m*, H-3′, H-4′ and H-5′) indicated that ring B was unsubstituted [5]; the singlet at δ 6 (2H, *s*) is characteristic of a methylenedioxy group, whilst the presence of two OMe groups was inferred by singlets at 4.12 (3H, *s*) and 3.87 (3H, *s*); a singlet at 6.65 (1H, *s*) was attributable to H-6 or H-8. The ^{13}C NMR (NORTD) spectrum presented 15 signals; besides the normal signals from the ring B carbon atoms [6], those corresponding to C-8 (94.8 ppm), C-9 (152.6 ppm), C-10 (119.6 ppm) [7], the methylenedioxy group (101.5 ppm) [8], OMe groups (59.4 and 60.6 ppm) and the carbonyl group (172.8 ppm) were easily distinguished.

A clue for the location of the OMe and methylenedioxy groups came from the MS; this gave a parent ion at *m/e* 326 (96%) which agrees with the empirical formula $C_{18}H_{14}O_6$; peaks at 325 (M^+ −1, base peak), 297 (M^+ −19, characteristic of a 3,5-dimethoxyflavone) [9], 194 (due to a fragment from ring A having one OMe and one methylenedioxy group) were indicative that no substituents were located at ring B. This was confirmed by ions at *m/e* 105 and 77 both due to an unsubstituted aromatic ring. According to these results, compound **1** has a OMe group attached at C-3 and the other substituents at ring A. Chemical proof for MeO-C_5 was obtained by demethylation with $AlCl_3$–K_2CO_3 in dry Et_2O yielding the phenolic product **2**, mp 186–188°; its UV (λ_{max} 323 and 273 nm) showed a bathochromic shift of band I on addition of $AlCl_3$ ($\Delta\lambda$I: 27.5 nm) indicating that it has a free OH group at C-5 while C-6 is occupied [10]. Methylation of **2** produces the original compound **1** showing that no isomerization had taken place during the demethylation reaction.

The position of the methylenedioxy group in **1** was assigned by analysis of the ^1H NMR in benzene-d_6: since no important shifts of the OMe signals were observed compared with those measured in $CDCl_3$, the position adjacent to the 5-OMe group must be occupied [11]. Hence, the methylenedioxy group should be attached to C-6 and C-7. It is noteworthy that a shift of the methylenedioxy signals is observed ($\delta_{CDCl_3} - \delta_{C_6D_6} = 0.89$); this is in agreement with a free 8-position.

EXPERIMENTAL

Mps are uncorr. UV were measured in EtOH, ^1H NMR at 60 MHz, ^{13}C NMR at 25.2 MHz, MS at 70 ev with a direct insertion probe. Microanalyses were performed by Dr. B. B. de Deferrari.

Plant material. Fresh plants of *G. martiana* Moquin were collected in the province of Salta (Argentina); voucher specimens were deposited at the CEFAPRIN herbarium under No. CP 457.

Extraction of plant and isolation of compound **1**. Dry whole plant (2.2 kg) was extracted with petrol (15 l.). The yellow ppt. obtained by concn of the extract was crystallized from EtOH to give white needles (0.1 g), mp 198–200°. UV λ_{max}nm: 313 and 269 (no changes were observed when $AlCl_3$, $AlCl_3$–HCl, NaOMe, NaOAc and NaOAc–H_3BO_3 were added). IR cm^{-1}: 1620, 1025, 1230, 930. ^1H NMR ($CDCl_3$, 90 MHz); δ 3.87 (3H, *s*, MeO-C_3), 4.12 (3H, *s*, MeO-C_5), 6.02 (2H, *s*, —OCH_2O—), 6.63 (1H, *s*, H-8), 7.43 (3H, *m*, H-3′, H-4′ and H-5′), 8 (2H, *m*, H-2′ and H-6′); (C_6D_6): δ 3.83 (3H, *s*, MeO-C_3), 4 (3H, *s*, MeO-C_5), 5.13 (2H, *s*, —OCH_2O—). ^{13}C NMR ($CDCl_3$, ppm): δ 59.4 and 60.6 (—OMe), 92.4 (C-8), 101.5 (—OCH_2O—), 119.6 (C-10), 127.4 (C-2′ and C-6′), 127.8 (C-3′ and C-5′), 129.6 (C-4′), 129.8 (C-1′), 133.8 (C-3), 140.0 (C-6 or C-7), 140.4 (C-6 or C-7), 151.8 (C-2 or C-9), 152.6 (C-2 or C-9), 172.7 (C-4). MS (*m/e*, %): 328 (M^+ +2, 2.6), 327 (M^+ +1, 18.0), 326 (M^+, 96.3), 325 (M^+ −1, 100), 307 (M^+ −1 −18, 29.4), 297 (M^+ −28, 37.0), 194 ($C_9H_6O_5$, 30.4), 164 (194 −30, 10.3), 105 (PhCO, 35.6), 77 (C_6H_5, 45.7). (Found: C, 66.21; H, 4.50. $C_{18}H_{14}O_6$ requires: C, 66.26; H, 4.30%).

5-*Hydroxy*-3-*methoxy*-6,7-*methylenedioxyflavone* (**2**). Compound **1** (47.8 mg) was demethylated with $AlCl_3$–K_2CO_3 in dry Et_2O according to ref. [12]. Yellow crystals of **2** were obtained from MeOH–C_6H_6, mp 186–188°. UV λ_{max}nm: 323, 273, 251 (sh); NaOMe: 288; $AlCl_3$: 350, 285; NaOAc: 286; NaOAc–H_3BO_3: 322, 273, 251 (sh). ^1H NMR ($CDCl_3$): δ 3.87 (3H, *s*, MeO-C_3), 6.08 (2H, *s*, —OCH_2O—), 6.53 (1H, *s*, H-8), 7.51 (3H, *m*, H-3′, H-4′ and H-5′), 8.05 (2H, *m*, H-2′ and H-6′), 12.85 (1H, *s*, HO-C_5). MS (*m/e*, %): 314 (M^+ +2, 2.7), 313 (M^+ +1, 18.2), 312 (M^+, 92.3), 311 (M^+ −1, 100), 294 (M^+ −18, 15.3), 293 (M^+ −1 −18, 14.1), 181 ($C_8H_5O_5$, 12.2), 180 ($C_8H_4O_5$, 19.3), 105 (PhCO, 54.1), 77 (Ph, 46.8). (Found: C, 65.46; H, 4.00. $C_{17}H_{12}O_6$ requires: C, 65.38; H, 3.85%).

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