$CHCl_3$–MeOH–MeCOEt (12:2:1) on polyamide TLC; purple color on paper in UV light to purple with UV + NH_3; mp 192–196°. UV spectral data: λ_{max}^{MeOH}; 240*s*, 290*s*, 342 nm; λ_{max}^{NaOMe}: 298, 353 nm; $\lambda_{max}^{AlCl_3}$: 330*s*, 372 nm; $\lambda_{max}^{AlCl_3/HCl}$: 315*s*, 366 nm; λ_{max}^{NaOAc}: 290*s*, 342 nm; $\lambda_{max}^{NaOAc/H_3BO_3}$: 290, 352 nm. The flavanone was separated by Si/gel TLC, C_6H_6–EtOAc–Me_2CO (8:1:1); R_f 0.86; purple on paper over UV light, remaining purple with NH_3. UV data: λ_{max}^{MeOH}: 290, 340 nm; λ_{max}^{NaOMe}: 293, 355 nm; $\lambda_{max}^{AlCl_3}$: 222, 314, 385 nm; $\lambda_{max}^{AlCl_3/HCl}$: 225, 314, 385 nm; $\lambda_{max}^{NaOAc/H_3BO_3}$: 291, 335 nm. MS: *m/e* 284 (M^+; 100%); *m/e* 207 (62%), *m/e* 180 (65%), *m/e* 104 (51%) and *m/e* 152 (69%).

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DIDYMOCARPIN, A NEW FLAVANONE FROM *DIDYMOCARPUS PEDICELLATA*

PRAKASH C. BOSE and NARAYAN ADITYACHAUDHURY

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswa Vidyalaya, Kalyani, Nadia, West Bengal, India

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Key Word Index—*Didymocarpus pedicellata*; Gesneriaceae; didymocarpin; 7-hydroxy-5,6,8-trimethoxyflavanone.

In continuation of our studies on the genus *Didymocarpus* [1–3], we further examined *D. pedicellata*, which elaborates a number of polymethoxylated chalcones, a flavanone and quinochalcones [4–7]. A new flavanone, didymocarpin, has now been isolated from the leaves of *D. pedicellata*, collected from the Western Himalayan regions [8]. It has been identified as 7-hydroxy-5,6,8-trimethoxyflavanone.

EXPERIMENTAL

The dried powdered leaves of *D. pedicellata* were successively extracted with petrol (bp 60–80°), C_6H_6 and $CHCl_3$. The C_6H_6 extract on chromatography over Si gel furnished a compound crystallizing from petrol–C_6H_6 as pale yellow needles, mp 103–104°, $[\alpha]_D$ −12.8° (c = 0.7, $CHCl_3$), $C_{18}H_{18}O_6$ (M^+ 330). The colour reaction (+ve Shinoda) coupled with the appearance of a double doublet (C_2-1H, 5.40 δ, J = 4 Hz) and a rough triplet (C_3-2H, 3.00 δ) in the NMR spectrum confirmed the presence of a flavanone system. Functional group analysis revealed the presence of three OMe groups (3H-singlets at 4.17, 3.97, 3.90 δ), a phenolic OH (1H-singlet at 5.57 δ, exchangeable with D_2O; γ_{max}^{KBr} 3430 cm^{-1}) and a conjugated $>C=O$ (γ_{max}^{KBr} 1680 cm^{-1}). The IR spectrum disclosed a complex aromatic substitution pattern (1600, 1460, 1430, 1360, 1300, 1240, 1170 cm^{-1}) and an unsubstituted benzene [6] ring (710, 630 cm^{-1}). A 5H-singlet at 7.47 δ indicated the presence of five aromatic protons. The two peaks at *m/e* 253 ($M^+ - 77$; $M^+ - C_6H_5$) and at *m/e* 226 ($M^+ - 104$; $M^+ - C_6H_5$—$CH{=}CH_2$) corresponding to the loss of phenyl and styrene fragments respectively from the M^+ ion confirmed that the B-ring is unsubstituted. Didymocarpin exhibited two other fragments at *m/e* 211 (*m/e* 226–15; *m/e* 226–Me) and *m/e* 183 (*m/e* 211–28; *m/e* 211–CO). The ready solubility of the flavanone in aq. Na_2CO_3 [9] coupled with the UV spectrum [λ_{max}^{EtOH} 282 (log ε 4.7) nm; $\lambda_{max}^{EtOH-0\ 1(N)NaOH}$ 296 (log ε 4.6) nm] showing a bathochromic shift of 14 nm suggested the presence of an —OH group in the 7-position of didymocarpin. The reduced activity of the 7-OH group towards NaOAc showing no bathochromic shift [$\lambda_{max}^{EtOH-NaOAc}$ 282 nm] of the maximum is presumably due to the presence of two oxygen substituents at 6 and 8 positions [10, 11]. The absence of a shift with $AlCl_3$ indicates that the 5-OH is methylated.

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A NEW FLAVONE GLYCOSIDE FROM THE LEAVES OF *PITYRODIA COERULEA*

J. B. HARBORNE* and C. I. STACEY†

*Phytochemical Unit, Department of Botany, The University of Reading, RG6 2AS, England; †Chemistry Department, Western Australian Institute of Technology, Bentley, Western Australia, 6102

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Key Word Index—*Pityrodia coerulea*, Verbenaceae; flavone; 6-hydroxyluteolin; 7-rhamnosylxyloside.

6-Hydroxyluteolin and its derivatives have rarely been found in the Verbenaceae [1]. There are two reports of it and its 6- and 3′-monomethyl ethers in *Lippia nodiflora* [2, 3]; and of the 6-glucoside of 6-hydroxylutcolin 7,3′-dimethyl ether in *Citharexylum subserratum* [4]. Both these plants are of Asian origin. In the course of a current survey of the flavonoids of the Western Australian Verbenaceae, we have isolated a new glycoside of 6-hydroxyluteolin which forms the major leaf flavonoid of *Pityrodia coerulea* Ewart & J. White. It appears to be a taxonomic marker for *Pityrodia coerulea* since it has not been found in any other species of the genus so far investigated. A number of other *Pityrodia* appear to have 6-hydroxyflavones or flavonols but these seem to occur with methylation rather than with sugar attachment.

The flavone glycoside was isolated as a yellow solid from the 70% ethanolic extraction of the dried leaves, and on acid hydrolysis yielded an aglycone and an equimolecular mixture of rhamnose and xylose (PC). The aglycone was identified as 6-hydroxyluteolin (NMR, MS, UV and co-chromatography). Spectral data suggested that the sugar molecules were attached as a disaccharide to the 7-position of the aglycone and this was confirmed by methylation of the glycoside with dimethyl sulphate followed by acid hydrolysis to give 7-hydroxy-3′,4′,5,6-tetramethoxyflavone. The partially methylated sugars obtained were 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3-di-*O*-methyl-D-xylose (PC). On the basis of these results, the glycoside was identified as 6-hydroxyluteolin 7-*O*-L-rhamnosyl-(1 → 4)-D-xyloside. Such a sugar combination does not appear to have been reported before in the flavone series [5], though a related flavonol, quercetin 3-rhamnosylxyloside (linkage unspecified) was found in *Tilia argentea* flowers by Hörhammer *et al.* [6].

EXPERIMENTAL

Isolation of the glycoside. The dried leaves were extracted with boiling 70% EtOH. The extract was concd and chromatographed Whatman 3MM paper using BAW. The major band (R_f 0.23) was yellow and was eluted with 80% MeOH The eluate was concd and chromatographed using 15% HOAc The major band (R_f 0.27) eluted with 80% MeOH and concd gave a yellow compound, mp 253–255° (decomp.). PC R_f values were 0.23 in BAW, 0.27 in 15% HOAc, 0.45 in BEW, 0.80 in Forestal and 0.50 in PhOH. UV max (nm) in MeOH were 260*sh*, 275, 302*sh*, 344 and spectral shifts with NaOH (band I, $\Delta\lambda$ +47), NaOAc (band II, +2), NaOAc + H_3BO_3 (band I, +32), $AlCl_3$ (band I, +96), $AlCl_3$ + HCl (band I, + 16) were observed In the MS the compound showed the presence of a parent ion at 302 ($C_{15}H_{10}O_7$ requires MW 302). The NMR spectrum (run in $CDCl_3$ as the acetate) gave signals centred at δ 7.58 (2′, 6′-H), 7.3 (5′-H), 6.94 (8-H), 6.53 (3-H), 3.92, 5.19 (sugars), 2.47, 2 36, 2.16, 2.02 (9 acetoxyl's), 1.17 (rhamnosyl Me).

Acid hydrolysis of glycoside. The glycoside in MeOH was hydrolysed with an equal vol. 2M HCl and the aglycone extracted with EtOAc. The aglycone was found to be 6-hydroxyluteolin (UV, NMR of acetate, co-chromatography) and the aq. residue was found to contain equimolecular amounts of rhamnose and xylose (co-chromatography) Hydrolysis carried out for periods up to 30 s resulted in the same products with no intermediate monoglycoside being found

Methylation of glycoside and hydrolysis of methylated product. The glycoside was methylated with Me_2SO_4–K_2CO_3 in Me_2CO for 36 hr and the methyl ether was hydrolysed with 2M HCl and the aglycone extracted with EtOAc. The aglycone was found to be 7-hydroxy-3′,4′,5,6-tetramethoxyflavone UV (max) in MeOH were 271, 328 and the spectral shift with NaOAc (band II, +10) was observed. The MS showed a parent ion at 358 ($C_{19}H_{18}O_7$ requires MW 358) and a major peak at 343 (—Me) which is characteristic of a methoxyl in the 6-position [7]. The partially methylated sugars were found to be 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3-di-*O*-methyl-D-xylose (PC) [8].

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