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A NEW NATURALLY OCCURRING FLAVANONE FROM *TETRAGONIA EXPANSA*

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Key Word Index—*Tetragonia expansa*; Aizoaceae; New Zealand spinach; 2,3-dihydro-7,8-dimethoxy-2-phenyl-4H-1-benzopyran-4-one; 7,8-dimethoxyflavanone.

Naturally occurring flavanoids which have a pyrogallol oxygenation pattern in the 'A' ring but no oxygenation in the 'B' ring are rare, there being only two reported examples to date. These are isolarrien (7-hydroxy-8-methoxyflavanone) and the corresponding chalcone larrien (2′,4′-dihydroxy-3′-methoxychalcone), both isolated from *Larrea nitida* [1]. We now report the occurrence of a third natural flavanoid with this unusual oxygenation pattern, 7,8-dimethoxyflavanone, isolated from New Zealand spinach (*Tetragonia expansa* Murr.).

The purified compound isolated from a toluene leaf extract of *Tetragonia expansa* fluoresced pale blue in 375 nm UV light and gave λ_{max} 284 nm (ε 16100). The IR spectrum showed strong absorption peaks at 1600 cm^{-1} (aryl) and 1690 cm^{-1} (aryl carbonyl) but no absorption over 3000 cm^{-1} (hydroxyl region). In the ^1H NMR spectrum the compound exhibited signals due to two methoxy groups δ 3.85 (3H, *s*) and 3.90 (3H, *s*), an *ortho* aromatic pair 6.60 (1H, *d*, J = 8 Hz) and 7.65 (1H, *d*, J = 8 Hz), five other aromatic protons 7.18–7.54 (5H, *m*) and a partly resolved three-proton ABX system at 5.56 (1H, *q*, J = 5, 10.5 Hz) and 2.79–3.20 (2H, *m*). The molecular formula was obtained from the MS which has M^+ 284.104985 (100%, $C_{17}H_{16}O_4$ requires 284.104850) and also prominent ions at *m/e* 180.044487 (78%, $C_9H_8O_4$ requires 180.042253), *m/e* 152.046028 (100%, $C_8H_8O_3$ requires 152.047339) and *m/e* 137 (24%).

These data strongly suggest that the compound is a flavanone, the chemical shifts of the three-proton ABX system being particularly characteristic of this type of flavanoid [2]. There are clearly two methoxy groups which from MS data must be sited on ring 'A' as the major fragmentation pathway is via a retro Diels–Alder reaction giving a prominent ion at *m/e* 180. This further fragments to give ions at *m/e* 152 and 137; a pattern agreeing very closely with that published for other flavanones [3]. The position of the methoxy groups on ring 'A' remains to be established but they must be substituted at positions which provide for a pair of aromatic protons exhibiting *ortho*-coupling in the ^1H NMR spectrum. Of the three available possibilities, the 7,8-substitution pattern is the most probable, since in this structure one proton is deshielded by the adjacent carbonyl and this would agree with the observed resonance at δ 7.65 in the present compound.

Confirmation of the proposed structure was by synthesis. Base-catalysed condensation of 2-hydroxy-3,4-dimethoxyacetophenone with benzaldehyde afforded a chalcone which was not isolated but cyclized under acid conditions to yield 7,8-dimethoxyflavanone. Comparison of the IR, UV and ^1H NMR spectra of the synthesized 7,8-dimethoxyflavanone and the isolated natural product showed the compounds to be identical. This was confirmed by TLC and GLC.

EXPERIMENTAL

UV spectra were recorded in EtOH, IR spectra in $CHCl_3$ and ^1H NMR spectra (100 MHz) in $CDCl_3$ using TMS internal standard. MS (70 eV) were determined using a direct insertion probe. Merck precoated plates Si gel 60 F254 were used for TLC.

Isolation. Leaves of New Zealand spinach (*Tetragonia expansa*) (5.5 kg fr. wt) were extracted in toluene (12 l. × 2) for 7 days. The combined extracts were reduced to 100 ml and waxes removed by precipitation with Me_2CO and filtration. The filtrate was evapd and the residue chromatographed on a PVP column eluted with toluene plus $CHCl_3$ (0–100%). The first fraction (fluorescent blue-green in 375 nm UV) was collected, evapd, the residue dissolved in toluene (30 ml) and more wax removed by Me_2CO precipitation and filtration. The wax-free fraction was evapd and the residue dissolved in toluene (50 ml) and applied to a Si gel (Merck kieselgel 40 Art. 10180 70–230 mesh ASTM) column, which was washed with $CHCl_3$ (2.5 l.) before elution with $CHCl_3$–EtOH (19:1). The flavanone band

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was further purified by TLC using the following elutants: (i) $CHCl_3$–EtOH (19:1) (R_f 0.66), (ii) *n*-hexane–Me_2CO (2:1) (R_f 0.38), (iii) isopropyl ether–toluene (3:1) (plate run × 6). In each case the compound was recovered by eluting from the Si gel with redistilled EtOAc. The final product was TLC pure in all the above systems and GLC gave a single peak on two columns: (i) 3% OV 17 on 80–100 mesh gaschrom Q at 250°, (ii) 2% SE-30 on 80–100 mesh gaschrom Q at 215° (yield 10 mg).

Synthesis of 7,8-dimethoxyflavanone. 2-Hydroxy-3,4-dimethoxyacetophenone was prepared by partial methylation of 2,3,4-trihydroxyacetophenone with Me_2SO_4 [4]. 2′-Hydroxy-3′,4′-dimethoxychalcone was prepared by a base-catalysed Aldol condensation similar to that described by ref. [5]. 2-Hydroxy-3,4-dimethoxyacetophenone (2.0 g) and freshly distilled PhCHO (2.0 g) were successively added with stirring to a soln of NaOH (4.0 g) in H_2O–EtOH (1:1) (35 ml) under N_2, at a temp. below 20°. The chalcone so formed was not isolated, but cyclized directly by diluting with H_2O (8 ml), acidifying by the slow addition of conc HCl (17 ml) with stirring and refluxed for 3 hr. The mixture was extracted with Et_2O (3 × 100 ml) and the extract washed with aq. Na_2CO_3, and H_2O, before evaporation. The residue was recrystallized from 100 to 120° petrol giving white needles of 7,8-dimethoxyflavanone (yield 1.0 g (35%), mp 115–116°).

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A NEW FLAVANONE GLYCOSIDE FROM THE STEM OF *HIBISCUS MUTABILIS*

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Key Word Index—*Hibiscus mutabilis*; Malvaceae; naringenin 5,7-dimethyl ether 4′-*O*-β-D-xylopyranosyl-β-D-arabinopyranoside.

Hibiscus mutabilis, commonly known as Guliajaib, has not been studied chemically but various parts of the plant are used medicinally [1, 2]. In the present study, a new flavanone glycoside, naringenin 5,7-dimethyl ether 4′-*O*-β-D-xylopyranosyl-β-D-arabinopyranoside, was identified from the stem tissue.

EXPERIMENTAL

The air-dried powdered stem of *Hibiscus mutabilis* was extd exhaustively with hot EtOH. The conc EtOH extract deposited a yellow ppt. after 2 days in the cold, which was retained for further study. The filtrate was diluted with H_2O, separated into 2 fractions and the H_2O sol. fraction extracted with increasingly polar organic solvents. The EtOAc extract gave the new flavanone glycoside which was crystallized from EtOAc–petrol and shown to be homogeneous by PC and TLC; mp 88–90°, $C_{27}H_{32}O_{13}$. (Found: C, 57.2; H, 5.17. Calc.: C, 57.44; H 5.67%). Acid hydrolysis of the glycoside (7% EtOH–H_2SO_4) gave naringenin 5,7-dimethyl ether, $C_{17}H_{16}O_5$. (Found: C, 67.72; H, 5.19. Calc.: C, 68.00; H, 5.33%). mp 140–1° (UV, IR, methoxyl) arabinose and xylose.

Alkaline degradation of the aglycone (50% EtOH–KOH) produced phloroglucinol dimethyl ether and *p*-hydroxybenzoic acid (mp, mmp and co-PC). The colour reactions, formation of phenyl hydrazone, negative Shinoda test, spectral data [UV λ_{max}^{MeOH} nm: 280, no shifts with various reagents, viz. NaOAc and NaOMe; IR ν_{max}^{KBr} cm^{-1}: 3350, 2850, 1685, 1600, 1510, 1460, 1360, 1280, 1170, 1120, 1020 and 825; NMR signals (in CCl_4 and TMS as an internal standard) (in ppm): δ 2.78 (H-3), 3.82 (5-OMe, 7-OMe), 5.15 (H-2), 5.87 (H-6), 6.0 (H-8), 6.82 (H-3′, H-5′) and δ7.12 (H-2′ and H-6′)] and the above chemical degradations of the glycoside indicated it to be a 5,7-dimethoxyflavanone glycoside.

The hydrolysability of the glycoside with almond emulsin (yielding both arabinose and xylose), the first appearance of xylose on partial acid hydrolysis (1% H_2SO_4), consumption of 3 mol periodate to produce 1 mol HCOOH per mol of glycoside, acid hydrolysis of the completely methylated glycoside (DMS/dry K_2CO_3) yielding 2,3-di-*O*-methyl arabinose (phenyl hydrazone and periodate oxdn.) and 2,3,4-tri-*O*-methyl xylose (mmp and co-chromatography with an authentic sample) indicated the sugar moiety to be β-D-xylopyranosyl-β-D-arabinopyranoside attached to the only 4′-free hydroxyl group present in the aglycone by a 1 → 4 linkage. Demethylation of the aglycone (50% HBr/HOAc) gave naringenin (UV, IR, R_f and co-PC). Hence the structure of the new flavanone glycoside has been assigned as naringenin 5,7-dimethyl ether 4′-*O*-β-D-xylopy-