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MINOR FLAVONOIDS OF *POLYGONUM NODOSUM*

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Key Word Index—*Polygonum nodosum*; Polygonaceae; flavonoids; kaempferol 3-*O*-glucoside-2″-gallate.

We have previously reported the identification of quercetin (**1**) and quercetin 3-*O*-glucoside-2″-gallate (**2**), which has molluscicidal activity, from the aerial parts of *Polygonum nodosum* Pers. [1]. Further investigation of the same plant has led to the isolation of three flavonoids by column chromatography and droplet counter-current chromatography. Two are known compounds, kaempferol (**3**) and quercetin 3-*O*-glucoside (**4**). The third compound (**5**) is a new flavonoid glycoside with a ^{13}C NMR spectrum similar to that of **2**. On hydrolysis of **5** with H_2SO_4, kaempferol and gallic acid were obtained and hydrolysis of **5** with NH_4OH gave a kaempferol glucoside which gave bathochromic shifts with both NaOAc and $AlCl_3$ in UV spectral analysis. These shifts are characteristic of a flavonol having a substituted hydroxyl group at C-3 [2]. From the ^{13}C NMR spectrum of **5**, the chemical shifts of C-2, C-3, and C-4 were typical for a flavonol 3-*O*-glycoside [1, 3]. These results indicate that the glucose is attached at C-3 of the kaempferol molecule. In the ^{13}C NMR spectrum of **5** and the ^1H NMR spectrum of the TMSi ether of **5**, the signals of the glucose moiety were identical with those of **2** and its TMSi ether, respectively [1], indicating that the galloyl group is attached to C-2 of the glucose. From these results, **5** was identified as kaempferol-3-*O*-*β*-D-glucopyranoside-2″-gallate.

EXPERIMENTAL

Isolation of flavonoids. The EtOH (33 l. × 3) extract of the aerial parts of *Polygonum nodosum* (29.8 kg) was concd and extracted with Et_2O, EtOAc, and *n*-BuOH, respectively. The EtOAc-soluble fraction was concd and chromatographed over Si gel using $CHCl_3$–MeOH as eluant giving compds **1** and **3** (19:1), **2**, **4**, and **5** (9:1–3:1). Compound **2** (20.4 g), the major component, and **1** were obtained by recryst. Compds **3**, **4** and **5** were isolated by DCCC ($CHCl_3$–MeOH–H_2O–*n*-BuOH, 10:10:6:1). Compound **2**, yellowish needles from EtOH–H_2O, mp 205°, $[\alpha]_D$ − 70.0° (*c* 1.0, MeOH), was identified as quercetin 3-*O*-glucoside-2″-gallate from spectroscopic data [1]. Compounds **1**, **3** and **4** were identified as quercetin, kaempferol, and quercetin 3-*O*-glucoside, respectively, by comparison with the IR spectra of authentic samples and their acetates.

Identification of kaempferol 3-O-glucoside-2″-gallate (**5**). Compound **5**, yellowish needles from MeOH–H_2O, mp 227–229°, $[\alpha]_D$ − 84.3° (*c* 1.0, MeOH); Found: C, 52.31; H, 4.12. $C_{28}H_{24}O_{15}\cdot\frac{5}{2}H_2O$ requires: C, 52.10; H, 4.53%; UV (MeOH): λ_{max} 269 (ε 27 400), 295 (sh), and 345 (sh, ε 16 800) nm; (+$AlCl_3$): 277.5, 302 (sh), 349, and 395; (+NaOAc): 271, 302, and 370 (sh) nm; IR (nujol): ν_{max} 3400, 1725, 1700, 1600, and 1360 cm^{-1}; ^{13}C NMR (100 MHz, DMSO-d_6): δ 61.1 (C-6″), 70.5 (C-4″), 74.6 (C-2″ and C-3″), 78.0 (C-5″), 94.1 (C-8), 98.6 (C-6), 99.1 (C-1″), 104.3 (C-10), 109.4 (C-2‴ and 6‴), 115.6 (C-3′ and 5′), 119.9 (C-1‴), 121.1 (C-1′), 131.2 (C-2′ and 6′), 132.8 (C-3), 138.7 (C-4‴), 145.7 (C-3‴ and 5‴), 156.6 (C-2 and 9), 160.3 (C-4′), 161.4 (C-5), 164.4 (C-7‴), 165.6 (C-7), and 177.4 (C-4).

TMSi ether of **5**. ^1H NMR (100 MHz, $CDCl_3$): δ 3.1–4.0 (4 H, *m*, H-3″, 4″, 5″, and 6″), 5.23 (1 H, *t*, *J* = 8 Hz, H-2″), 5.90 (1 H, *d*, *J* = 8 Hz, H-1″), 6.27 (1 H, *d*, *J* = 2 Hz, H-6), 6.36 (1 H, *d*, *J* = 2 Hz, H-8), 6.94 (2 H, *d*, *J* = 9 Hz, H-3′ and 5′), 7.34 (2 H, *s*, H-2‴ and 6‴), and 8.07 (2 H, *dd*, *J* = 9 and 3 Hz, H-2′ and 6′).

Hydrolysis of **5**. (i) Acid hydrolysis. To **5** (3 mg) were added 7% H_2SO_4 (1 ml) and EtOH (1 ml) and the mixture was refluxed for 1 hr. Gallic acid and kaempferol were identified by TLC with authentic samples although glucose could not be detected. (ii) *Alkaline hydrolysis.* To **5** (200 mg) were added 0.1 N NH_4OH (40 ml) and MeOH (10 ml) and the mixture allowed to stand for 2 days at room temp. The reaction mixture was concd and chromatographed by DCC to give a flavonol glycoside (UV (MeOH): λ_{max} 267, 302 (sh), and 349 nm; (+$AlCl_3$): 275, 305, 351, and 400 nm; (+NaOAc): 275.5, 305, and 360 nm) which on *β*-glucosidase hydrolysis gave kaempferol and glucose.

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