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BREVICORNIN, A FLAVONOL FROM *EPIMEDIUM BREVICORNUM*

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Key Word Index—*Epimedium brevicornum*; Berberidaceae; flavonol; brevicornin.

Abstract—A new flavonol, brevicornin, with a 3″-methoxy-isopentyl group, was isolated from the aerial parts of *Epimedium brevicornum*. Its structure was determined to be 3,5,7-trihydroxy-4′-methoxy-8-(3″-methoxyisopentyl)flavone. Four known flavonoids epimedin B, epimedin C, β-anhydroicaritin and tricin were also isolated from the same plant.

INTRODUCTION

Epimedium brevicornum Maxim. is widely distributed in northern China and used as a tonic in traditional Chinese medicine. In this paper, a new flavonol, brevicornin (**1**), along with four known flavones (**2**–**5**) are reported from the aerial parts.

RESULTS AND DISCUSSION

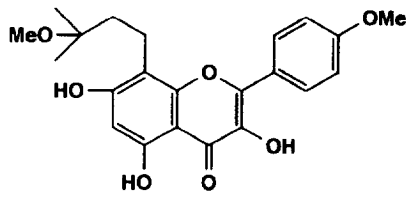
Compounds **1**–**5** were isolated from the *n*-butanol soluble fraction of the 95% ethanol extract of the aerial parts of *E. brevicornum* by means of chromatography on silica gel and polyamide. Compound **1** was obtained as yellow needles, mp 198–200°. The molecular formula of **1** was established from the molecular ion at *m/z* 400.1525 (calc. for $C_{22}H_{24}O_7$ 400.1521) in the HR mass spectrum. Its UV spectrum showed absorption bands of a typical flavonol at 272, 320 and 372 nm, which exhibited bathochromic shifts by the addition of shift reagents (sodium methoxide, sodium acetate and $AlCl_3$), indicating the presence of hydroxyl groups at C-3, C-5 and C-7 and the absence of a free hydroxyl group at C-4. These were confirmed by proton signals at 12.32 (C_5-OH), 10.66(C_7-OH) and 9.47(C_3-OH). From the ^{1}H and ^{13}C NMR spectral data, it was found that **1** was similar to anhydroicaritin [1, 2] except for a five-carbon unit linked to C-8 and a methoxyl group. In the ^{1}H NMR spectrum, there were two benzylic proton signals at δ2.72 (2H, *m*, H-1″), another multiplet at δ1.59 assigned to the methine protons (2H, *m*, H-2″), and six methyl protons appearing in singlet at δ1.16 assigned to H-4″, 5″, which suggested no double bond between C-2″ and C-3″. The above assignments were confirmed by the ^{13}C NMR spectrum: δ38.0(C-1″), 16.7(C-2″) and 24.8(C-4″, 5″). The signals of methoxyl protons in the ^{1}H NMR spectrum, δ3.14(3H, *s*), must be assigned to 3″-OMe, while the C-3″ signal in the ^{13}C NMR spectrum corresponded to δ73.7. The HR mass spectrum gave the $[M]^+$ and base peak for 400.1525 (calc. 400.1521) and 368.1281 (calc. 368.1259), which suggested that a fragment of methanol was removed. The other fragments in the mass spectrum at *m/z* 353, 313, 300, 165 and 135 were the same as those for anhydroicaritin. Thus, **1** must be 3,5,7-trihydroxy-4′-methoxy-8-(3″-methoxyisopentyl)flavone.

The structure of the four known flavonols isolated were identified as epimedin B[2], epimedin C[3], β-anhydroicaritin (**4**) [4] and tricin[2].

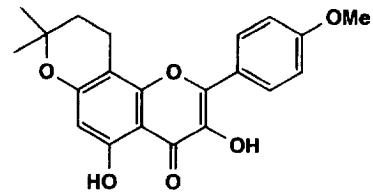
EXPERIMENTAL

Extraction and isolation. The dried and powdered aerial parts of *E. brevicornum* (4.5 kg) were extracted (× 3) with 95% EtOH under reflux for 2 hr. The combined extracts were concd under reduced pressure. The residue (440 g) was suspended in H_2O and extracted successively with CH_2Cl_2, EtOAc and *n*-BuOH. The *n*-BuOH fraction (120 g) was submitted to CC on polyamide (eluent: EtOH–H_2O, gradient) and sepd into five parts. Compounds **1** (25 mg), **4** (33 mg) and **5** (29 mg) from part 5, and **2** (379 mg) and **3** (420 mg) from part 2 were obtained via CC on silica gel and polyamide with $CHCl_3$–MeOH as eluent (gradient), and purified on Sephadex LH-20 eluted with MeOH.

Compound **1**. Yellow needles (MeOH). mp 198–200°; UV λ_{max}^{MeOH}nm: 272, 320, 372; + NaOMe: 283, 307, 419; + $AlCl_3$: 273, 352, 431; + $AlCl_3$/HCl: 273, 315, 352, 431; + NaAc: 273, 313, 353, 428; + NaOAc/H_3BO_3: 273, 316, 375. EI-MS *m/z* (rel. int.): 400 (24), 368 (100), 353 (74), 313 (84), 300 (28), 165 (8), 135 (12). ^{1}H NMR (300 MHz, DMSO-d_6): δ1.16 (6H, *s*, H-4″, 5″), 1.58 (2H, *m*, H-2″), 2.72 (2H, *m*, H-1″), 3.14 (3H, *s*, 3″-OMe), 3.84 (3H, *s*,



1 brevicornin



4 β-anhydroicaritin

Table 1. ^{13}C NMR spectral data for 1 and 4 (DMSO-d_6)

C	1	4
2	157.7	157.5
3	135.6	136.1
4	176.0	175.8
5	158.0	157.9
6	97.6	98.5
7	160.3	159.1
8	103.0	103.8
9	153.3	153.0
10	106.4	105.6
1′	123.3	123.3
2′,6′	129.1	129.1
3′,5′	113.9	114.0
4′	161.0	160.3
1″	38.0	31.0
2″	16.7	15.7
3″	73.7	76.2
4″	24.8	26.3
5″	24.8	26.3
4′-OCH_3	55.4	55.3
3″-OCH_3	48.7	—

4′-OMe), 6.28 (1H, *s*, H-6), 7.07 (2H, *d*, J = 9.0Hz, H-3′, 5′), 8.16 (2H, *d*, J = 9.0Hz, H-2′, 6′), 9.47 (1H, *s*, C_3-OH), 10.66 (1H, *s*, C_7-OH), 12.32 (1H, *s*, C_5-OH). ^{13}C NMR (75 MHz) spectral data: Table 1.

Compound **4**. Yellow needles (MeOH). mp 217–220°; UV λ_{max}^{MeOH}nm: 271, 316, 348. EI-MS (*m/z*): 368, 353, 313, 300. ^{1}H NMR (300 MHz, DMSO-d_6): δ1.32 (6H, *s*, 4″, 5″-Me), 1.85 (2H, *t*, J = 6.6 Hz, H-2″), 2.84 (2H, *t*, J = 6.6 Hz, H-1″), 3.83 (3H, *s*, 4′-OMe), 6.13 (1H, *s*, H-6), 7.12 (2H, *t*, J = 9.0 Hz, H-3′, 5′), 8.16 (2H, *d*, J = 9.0 Hz, *s*, H-2′, 6′), 9.59 (1H, *s*, C_3-OH), 12.18 (1H, *s*, C_5-OH), ^{13}C NMR (75 MHz) spectral data: Table 1.

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