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TWO FLAVANONES FROM THE ROOT BARK OF *LESPEDEZA DAVIDII*

MINGSHI WANG, JINGRONG LI and WEIGUO LIU

Department of Phytochemistry, Nanjing College of Pharmacy, Nanjing, People's Republic of China

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Key Word Index—*Lespedeza davidii*; Leguminosae; lespedezaflavanone A; lespedezaflavanone B; 6,8-di-γ,γ-dimethylallyl-4′-methyoxy-5,7,2′-trihydroxy-(2*S*)-flavanone; 8,3′-di-γ,γ-dimethylallyl-5,7,4′-trihydroxy-(2*S*)-flavanone.

Abstract—Two new flavanones have been isolated from the root bark of *Lespedeza davidii* and their structures established as 6,8-di-γ,γ-dimethylallyl-4′-methyoxy-5,7,2′-trihydroxy-(2*S*)-flavanone and 8,3′-di-γ,γ-dimethylallyl-5,7,4′-trihydroxy-(2*S*)-flavanone on the basis of spectroscopic evidence.

INTRODUCTION

The roots and leaves of *Lespedeza davidii* Franch., which grows in Zhejiang province have been used as a Chinese drug, he-xue-dan, for the treatment of dysentery and fever [1]. Two new flavanones, named lespedezaflavanone A (1) and lespedezaflavanone B (2), have been isolated from the root bark and their structural elucidation is now described.

RESULTS AND DISCUSSION

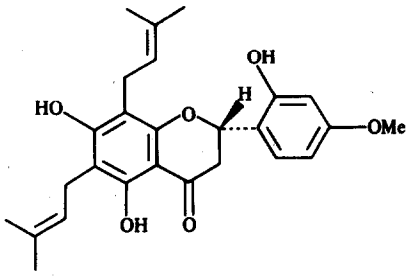
Lespedezaflavanone A (1), (M^+ = 438.2059 $C_{26}H_{30}O_6$, $[\alpha]_D^{11.5}$ −60° *c* = 0.250 $CHCl_3$), was obtained as yellow needles, mp 157–158° and gave a positive Mg–HCl test. The IR spectrum of 1 showed strong absorptions at 1640 cm^{-1} (chelated C=O group) and 3400 cm^{-1} (OH). The UV spectrum (λ_{max}^{MeOH} nm = 295, 345 (sh)) suggested a flavanone structure [2]. The proton magnetic resonance (^{1}H NMR) spectrum of 1 showed δ6.30, 6.41 and 12.35 (each 1H *s* disappeared on the addition of D_2O, OH × 3), δ2.85 (1H *dd J* = 2.9, 17.3 Hz C_3-βH), δ3.15 (1H *dd J* = 17.3, 13.0 Hz C_3-αH), δ5.52 (1H *dd J* = 2.9, 13.0 Hz C_2-H) [3]. It also indicated the presence of two γ,γ-dimethylallyl groups [δ1.69, 1.70, 1.74, 1.81 (each 3H *s* CH_3 × 4), δ3.27, 3.34 (each 2H *d J* = 7.0 Hz Ar–CH_2–CH= × 2), δ5.13, 5.22 (each 1H *m* CH_2–CH= × 2] [4], a methoxy group (δ3.78 3H *s*) and three aromatic protons [δ7.10 (1H *d J* = 8.5 Hz C_6-H), δ6.50 (1H *dd* J = 8.5, 2.5 Hz C_5-H), δ6.47 (1H *d J* = 2.5 Hz C_3-H)].

In the MS of 1, the ion peak at *m/z* 420 was derived from M − H_2O (chelated C_2-OH) [5]. The ion peaks at *m/z* 288 and 150 were derived from a retro-Diels–Alder fragmentation. In view of the ^{1}H HMR spectral data, the ion peak at *m/z* 288 must include the A-ring. It loses C_4H_7 to yield the ion peak at *m/z* 233 and losses C_4H_8 again to yield the ion peak at *m/z* 177 and, therefore, the A-ring contains two γ,γ-dimethylallyl groups. On the other hand, the ion peak at *m/z* 150 arises from the B-ring. It loses CH_3 to yield the ion peak at *m/z* 135 and, therefore, the B-ring contains a methoxy group.

Positive shifts in the UV spectrum after the addition of sodium acetate and aluminium chloride indicated that the two hydroxy groups at C-5, C-7 were free and since the ^{1}H NMR spectrum (B-ring) of 1 showed ABX type proton signals of the aromatic ring the methoxy group must be located at C-4.

From these data, the structure 6,8-di-γ,γ-dimethylallyl-4′-methoxy-5,7,2′-trihydroxyflavanone was assigned to 1. As the specific optical rotation of 1 had a minus (−) sign and the ^{1}H NMR spectrum showed an *aa* coupling constant of C_2, C_3-H, like those of other natural flavanones [6], 1 must have an (*S*)-configuration at C-2.

Lespedezaflavanone B (2) (M^+ = 408.1915 $C_{25}H_{28}O_5$, $[\alpha]_D^{16}$ −29.13° *c* = 0.515 MeOH) was isolated as colourless needles, mp 141–142°. It gave a negative Gibbs reaction and a positive Mg–HCl test. The IR spectrum of



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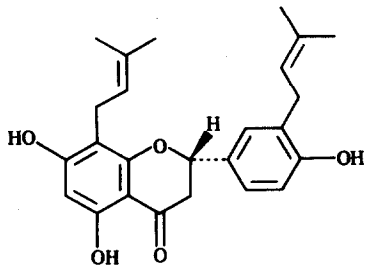

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2 showed strong absorptions at 1630 cm^{-1} (chelated C=O group) and 3300 cm^{-1} (OH). The UV spectrum [λ_{max}^{MeOH} nm = 293, 340(sh)] suggested a flavanone structure.

The proton magnetic resonance spectrum of 2 showed δ5.30 (1H *dd* J = 13.0, 2.8 Hz C_2-H), δ3.04 (1H *dd* J = 17.1, 13.0 Hz C_3-αH), δ2.76 (1H *dd* J = 17.1, 2.8 Hz C_3-βH) attributed to the C-ring protons [3]. It also indicated the presence of two γ,γ-dimethylallyl groups δ1.77, 1.71 (each 6H) *s* $(CH_3)_3 \times 2$], δ3.37, 3.29 (each 2H *d* J = 7.0 Hz Ar–C$\underline{H}_2$–CH= × 2), δ5.31, 5.19 (each 1H *m* CH_2–C$\underline{H}$= × 2), three hydroxy groups [δ12.00, 6.20 and 5.32 (each 1H s) which shifted in DMSO-d_6 to δ12.10, 10.75 and 9.50] and four aromatic protons [δ6.00 (1H *s* C_6 or C_8-H), δ6.83 (1H *d* J = 7.8 Hz C_5·-H), δ7.18 (2H *m* C_2· and C_6·-H)].

In the MS of 2, the ion peaks at m/z 220 and 188 were derived from a retro-Diels–Alder fragmentation. In view of the ^{1}H NMR spectral data, the ion peak at m/z 220 must include the A-ring. It loses C_4H_7 to yield the ion peak at m/z 165 and, therefore, the A-ring contains one γ,γ-dimethylallyl group. On the other hand, the ion peak at m/z 188 arises from the B-ring. It loses C_4H_7 to yield an ion peak at m/z 133, therefore the B-ring must also contain one γ,γ-dimethylallyl group. There are thus two γ,γ-dimethylallyl groups in 2 one attached to the A-ring and the other to the B-ring.

Positive UV shifts after the addition of sodium acetate, and aluminium chloride indicated that the three hydroxyl groups at C_5, C_7 and C_4· were free and therefore the γ,γ-dimethylallyl group in the A-ring must be at C_8 [7]. Since the ^{1}H NMR spectrum (B-ring) of 2 showed ABX type proton signals of the aromatic ring, the γ,γ-dimethylallyl group in the B-ring must be located at C_3.

From the above analysis, the structure of 2 was concluded to be 8,3′-γ,γ-dimethylallyl-5,7,4′-trihydroxyflavanone. Since the specific optical rotation of 2 had a minus (−) sign, and the ^{1}H NMR spectrum showed an aa coupling (J = 13.0 Hz) of C_2, C_3-H, like those of other natural flavanones, 2 most probably has an (*S*)-configuration at C-2.

EXPERIMENTAL

All mps are uncorr. ^{1}H NMR spectra were measured at 400 MHz with a Bruker AM-400 spectrometer; chemical shifts are given on the ppm scale with tetramethylsilane as an int. standard (*s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet; *br*, broad).

CC was carried out on silica gel (120–160 mesh) and TLC on silica gel G_{F254}. Spots on TLC were visualized by spraying with phosphomolybdic acid and heating. The following solvent systems were employed: solvent A: C_6H_6–Me_2CO (4:1); solvent B: C_6H_6–ethyl formate (9:1).

Extraction and isolation. Dried root bark of *Lespedeza davidii* was extracted with EtOH and the EtOAc soluble portion separated on a silica gel column, eluted with cyclohexane–EtOAc. The fraction from 9:1 was recrystallized from a mixture of petrol and EtOAc to give 1. The fraction from 8:1 was recrystallized from C_6H_6 to give 2.

Lespedezaflavanone A. (1). Green–brown with $FeCl_3$, positive Gibbs reaction. $[\alpha]_D^{11.5}$ −60° c = 0.250 $CHCl_3$ MS m/z: 438.2059 (M^+ $C_{26}H_{30}O_6$ 47.2%), 420 (47.16%), 405 (10.83%), 377 base peak (100%), 365 (32.45%), 321 (26.51%), 309 (25.30%), 233 (34.81%), 288 (3.30%), 273 (13.58%), 189 (52.47%), 177 (44.46%), 150 (21.37%), 135 (11.26%). UV λ_{max}^{MeOH} nm (log ε): 295 (4.22), 345 (3.58) (sh); + NaOMe 340 (4.45); + $AlCl_3$ 315 (4.25); + $AlCl_3$ + HCl 315 (4.25), 400 (3.45); + NaOAc 341 (4.36); + NaOAc + H_3BO_3 295 (4.16); 341 (3.86). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1640 (C=O), 1620, 1520 (arom. C=C), 1380, 1360 $(CH)_3$. ^{1}H NMR ($CDCl_3$): δ6.30, 6.41 (each 1H, *s* OH × 2; disappeared on the addition of D_2O), δ12.35 (1H *s* C_5-OH; disappeared on the addition of D_2O), δ2.85 (1H *dd* J = 2.9, 17.3 Hz C_3-βH), δ3.15 (1H *dd* J = 17.3, 13.0 Hz C_3-αH), δ5.52 (1H *dd* J = 2.9, 13.0 Hz C_2-H), δ1.69, 1.70, 1.74, 1.81 (each 3H *s* CH_3 × 4), δ3.27, 3.34 (each 2H *d* J = 7.0 Hz Ar–C$\underline{H}_2$–CH= × 2), δ5.13, 5.22 (each 1H *m* Ar–CH_2–C$\underline{H}$= × 2), δ3.78 (3H *s* OCH_3), δ7.10 (1H *d* J = 8.5 Hz C_6·-H), δ6.50 (1H *dd* J = 8.5, 2.5 Hz C_5·-H), δ6.47 (1H *d* J = 2.5 Hz C_3·-H). The relationship of corresponding protons was confirmed by proton spin-decoupling.

Lespedezaflavanone B (2). Green–brown with $FeCl_3$. Gibbs reaction (−). Mg–HCl (+). $[\alpha]_D^{16}$ −29.13° c = 0.515 MeOH. MS m/z: 408.1915 (M^+ $C_{25}H_{28}O_5$ 92.78%), 393 (13.48%), 365 (20.78%), 353 (29.26%), 233 (11.40%), 221 (23.31%), 220 (27.34%), 203 (15.37%), 192 (52.33%), 188 (15.81%), 177 (42.37%), 165 base peak (100%), 133 (38.16%). UV λ_{max}^{MeOH} nm (log ε): 293 (4.20), 340 (sh) (3.57); + NaOMe 332 (4.40), + $AlCl_3$ 316 (4.35), 392 (3.57); + $AlCl_3$ + HCl 313 (4.31), 392 (3.57); + NaOAc 332 (4.28); + NaOAc + H_3BO_3 293 (4.23), 333 (3.87). IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1630 (C=O), 1600, 1500 (arom. C=C), 1390, 1370 (CH_3). ^{1}H NMR ($CDCl_3$): δ5.30 (1H *dd* J = 13.0, 2.8 Hz C_2-H), δ3.04 (1H *dd* J = 17.1, 13.0 Hz $C_{3\alpha}$-H), δ2.76 (1H *dd* J = 17.1, 2.8 Hz C_3-βH), δ1.77, 1.71 [each 6H s $(CH_3)_2 \times 2$], δ3.37, 3.29 (each 2H *d* J = 7.0 Hz Ar–C$\underline{H}_2$–CH × 2), δ5.31, 5.19 (each 1H *m* Ar–CH_2–C$\underline{H}$= × 2), δ12.00 (1H *s* C_5-OH), δ6.20, 5.32 (each 1H *s* shifted in DMSO-d_6 to δ10.75 and 9.50 C_7-OH and C_4·-OH), δ6.00 (1H *s* C_6-H), δ6.83 (1H *d* J = 7.8 Hz C_5·-H), δ7.18 (2H *m* C_2· and C_6·-H). The relationship of corresponding protons was confirmed by proton spin-decoupling.

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