Four New Neoclerodane-Type Diterpenoids, Scutellones B, G, H, and I, from Aerial Parts of *Scutellaria rivularis*

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Four new neoclerodane-type diterpenoids, scutellones, B, G, H, and I, have been isolated from aerial parts of *Scutellaria rivularis* WALL., and their structures elucidated on the basis of spectral and chemical evidence.

Keywords *Scutellaria rivularis*; Labiatae; neoclerodane-type diterpenoid; scutellone B, G, H, I

"Ban zhi lian" (dried whole plants of *Scutellaria rivularis* WALL., Labiatae) has been used in folk medicine for the treatment of tumors, heptitis, liver cirrhosis and other diseases in China and Taiwan.[1] The chemical constituents of this plant have been investigated in detail: more than thirty kinds of flavonoids, including unknown bisflavones, unknown alkaloids, triterpene acids, and monolignols, as well as sterol glucosides,[2] have been isolated. The ethanol extract from aerial parts of this plant was separated on a silica gel column, followed by Sephadex LH-20 column chromatography to give six neoclerodane-type diterpenoid lactones (scutellones A, B, C, D, E, and F), one new oleanane-type triterpenoid (scutellaric acid) and eighteen flavonoid constituents.[2f,h] The structures of scutellones A, B, C, D, E, F, and scutellaric acid were elucidated as **1a**,[3] **1b**,[4] **1c**,[5] **2a**,[6] **2b**,[6] **3**[5] and **4**,[7] respectively. Rencently, Tomimori *et al.* reported the isolation of five clerodane type diterpenoids, scuterivulactones A, B, C_1, C_2, and D from the same source. The structures of scuterivulactones C_1, C_2,[8] and D[9] were identical with scutellone A (**1a**),**5a**, and scutellone D (**2a**), respectively. We have reinvestigated the extract and carried out a detailed separation. Three new neoclerodane-type diterpenoids, scutellones G (**5b**), H (**2c**), and I (**2d**), were isolated. The structural elucidation of scutellones B (**1b**)[4] and G (**5b**)[10] was reported in brief communications. In this full paper we describe our study of the structures of scutellones H and I in addition to scutellones B and G.

Scutellone B (**1b**), needles from acetone, has the molecular formula $C_{29}H_{36}O_8$ on the basis of elementary analysis and the mass spectrum (MS) [M^+ peak at *m/z* 512 and fragment ion peaks at 390 ($M^+ - C_6H_5COOH$, 100%), 330 ($M^+ - C_6H_5COOH - CH_3COOH$), 122 ($C_6H_5COOH$), and 105 ($C_6H_5CO$), indicating one benzoate and one acetate]. The ultraviolet (UV) absorption bands of **1b** supported the presence of benzoate and the infrared (IR) absorption

TABLE I. ^{1}H-NMR Data for Scutellones B (**1b**), G (**5b**), H (**2c**) and I (**2d**) (300 MHz, $CDCl_3$)

H	1b	5b	2c	2d
3			3.76 br s	3.81 br s
6	5.70 m	5.42 m	6.02 dd (11.4, 5.1)	5.96 dd (11.1, 5.4)
10			2.70 d (12.3)	2.66 d (11.4)
11	5.70 m	5.42 m	6.38 d (16.3)	6.38 d (16.5)
12			6.35 d (16.3)	6.35 d (16.5)
14	2.83 s	2.62, 3.05 d (17.0)	5.86 br s	5.86 br s
16	4.77, 4.39 d (10.9)[a]	4.24, 4.44 d (9.0)	5.02 br s	4.99 br s
17	1.35 s	1.29 s	1.44 s	1.45 s
18	0.90 d (6.6)	0.88 d (6.8)	1.26 s	1.26 s
19	1.02 s	1.03 s	1.01 s	1.02 s
20	1.07 s	1.08 s	1.10 s	1.06 s
3′	7.97 d (7.7)	7.96 dd (8.0, 1.5)	8.00 d (7.1)	8.00 dd (7.3, 1.2)
4′,5′	7.4—7.6 m	7.4—7.6 m	7.4—7.6 m	7.4—7.6 m
MeCO–	2.09 s	2.10 s		
MeO–				3.20 s
MeCH$_2$O–			1.66 t (7.0)	
MeCH$_2$O–			3.38 m	

a) Figures in parentheses are coupling constants in Hz.

TABLE II. ^{13}C-NMR Data (δ Values) for Scutellones B (**1b**), G (**5b**), H (**2c**) and I (**2d**)

C	1b	5b	2c	2d
1	22.7 t	22.9 t	17.4 t	17.5 t
2	40.9 t	41.0 t	29.6 t	29.7 t
3	210.5 s	210.8 s	75.1 d	75.3 d
4	57.3 d	57.5 d	72.5 s	72.8 s
5	46.0 s	46.2 s	46.5 s	45.7 s
6	74.9 d	75.3 d	75.4 d	75.4 d
7	37.8 t	37.9 t	37.9 t	37.9 t
8	81.5 s	81.6 s	77.2 s	76.9 s
9	42.6 s	42.9 s	48.7 s	48.5 s
10	43.1 d	43.3 d	39.2 d	40.0 d
11	72.8 d	73.1 d	149.4 d	150.1 d
12	35.1 t	34.9 t	121.3 d	120.7 d
13	76.6 s	77.8 s	162.5 s	162.0 s
14	42.5 t	43.9 t	114.2 d	113.1 d
15	173.3 s	172.8 s	173.3 s	173.2 s
16	78.9 t	77.1 t	70.9 t	70.6 t
17	20.9 q	21.1 q	26.5 q	26.3 q
18	9.5 q	9.7 q	15.9 q	16.0 q
19	10.0 q	10.3 q	12.8 q	12.7 q
20	16.5 q	16.6 q	15.7 q	15.3 q
1′	164.1 s	165.3 s	165.5 s	165.0 s
2′	130.4 s	130.4 s	130.9 s	130.5 s
3′	129.2 d	129.4 d	129.5 d	129.3 d
4′	128.2 d	128.4 d	128.4 d	128.4 d
5′	132.9 d	133.1 d	132.9 d	132.6 d
MeCO–	169.5 s	170.1 s		
MeCO–	23.7 q	24.0 q		
MeO–				56.7 q
MeCH$_2$O			16.5 q	
MeCH$_2$O			57.4 t	

Run in $CDCl_3$ at 300 MHz; s, singlet; d, doublet; t, triplet; q, quartet. Assignments established by off-resonance and DEPT methods.

spectrum revealed γ-lactone (1780 cm^{-1}), ester (1740 cm^{-1}), and ketone (1715 cm^{-1}), absorptions. The proton and carbon-13 nuclear magnetic resonance (^1H- and ^{13}C-NMR) signals are listed in Tables I and II, respectively. A comparison of the spectral data of scutellone A (**1a**) and scutellone B (**1b**) suggested that scutellone B (**1b**) possessed the same structural skeleton as scutellone A (**1a**) with the exception of the presence of one ketone group in place of an α-glycol function. This assignment was further supported by the fact that **1b**, on treatment with *p*-toluenesulfonic acid in isopropenyl acetate at room temperature overnight, gave the enol acetate (**6**) (mp 243—245 °C). The enol acetate (**6**) exhibited six methyl groups at δ 1.03, 1.31, 1.42, 2.05, 2.05, and 2.07 (each 3H, s), and the doublet signal at δ 0.90 in **1b** disappeared. Partial saponication of **1b** was performed by treatment with 1 N methanolic NaOH solution for 2 h at room temperature, giving the monoalcohol (**7**) [mp 268—270 °C; ν_{max} 3480 cm^{-1}; δ $CDCl_3$ 4.18 (1H, dd, J=10.5, 4.5 Hz, H-11)], which was subsequently acetylated with Ac_2O and pyridine to yield **1b**. This result confirmed that the C-4 methyl group was located in a stable α-equatorial orientation. Chemical correlation between scutellone B (**1b**) and scutellone A (**1a**) was achieved as follows. When scutellone A (**1a**) was treated with *p*-toluenesulfonic acid in $CHCl_3$ at 50—55 °C for 2 h, scutellone B (**1b**) was isolated after purification. The result confirmed the structure of scutellone B (**1b**) as a new neoclerodane-type diterpenoid. The mechanism of this transformation is proposed to be as shown in Chart 1.

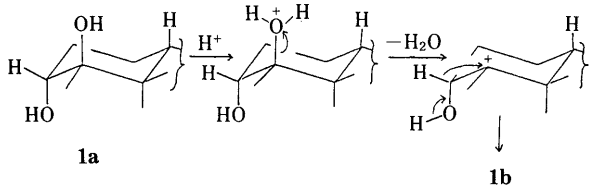

Chart 1

Scutellone G (**5b**), needles from acetone, has the molecular formula $C_{29}H_{36}O_8$ on the basis of elementary analysis and the MS [M^+ peak at m/z 512 and fragment ion peaks at 390, 330, 122 and 105 (100%)]. The UV spectrum of **5b** indicated benzoate and the IR spectrum revealed γ-lactone (1780 cm^{-1}), ester (1740 cm^{-1}), and ketone (1715 cm^{-1}) absorptions, as in **1b**. The ^1H–^{13}C and ^1H–^1H correlation spectroscopy (COSY) spectra clarified the oxo function at C-3. By comparison of the ^1H-NMR (Table I) and ^{13}C-NMR (Table II) spectra of scutellone G (**5b**) and scutellone B (**1b**), **5b** was concluded to be the 13-epimer of **1b**. This was supported by the nuclear Overhauser effect (NOE) experiment, in which NOE's were observed between H-16 and H-17 (4.0% enhancement) as well as between H-11 and H-17 (2.4% enhancement).[8] Compound **5b** possessed the same γ-lactone configuration as in **5a** but different from that in **1a**, **1b** and **1c**, based on a comparison of the chemical shift of H-14 in **1a** (δ 2.74 and 2.79), **1b** (δ 2.83), **1c** (δ 2.72 and 2.81), **5c** (δ 2.64 and 3.04) (prepared from **5a**),[11] and **5b** (δ 2.62 and 3.05). The above conclusion was also confirmed by comparison of the chemical shift of C-14 in **1a** (δ 42.5),[3] **1b** (δ 42.5), **1c** (δ 42.7),[5] **5b** (δ 43.9) and **5c** (δ 43.7).[11] Sodium borohydride reduction of **5b** gave only the triol (**8a**) [mp 234—236 °C; ν_{max}: 3400 cm^{-1}; δ $CDCl_3$: 3.50—3.80 (5H, m)] which was subsequently acetylated and yielded the tetraacetate **8b** [amorphous; ν_{max} 1735 and 1710 cm^{-1}; δ $CDCl_3$ 2.04, 2.05, 2.06, and 2.09 (each 3H, s), 4.11 (2H, s, H-16), 4.35 (2H, m, H-15), and 4.86 (1H, br s, H-3)]. This result showed that the ketone and lactone moieties were reduced by sodium borohydride. It is well-known that esters or lactones are essentially inert to reduction by sodium borohydride. In fact, esters or lactones containing a participating neighboring group[12] as well as some heterocyclic esters[13] can be converted into the corresponding alcohols. The mechanism of this reduction is proposed to be as shown in Chart 2. The hydroxyl group located at the C-3

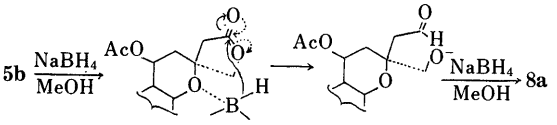

Chart 2

position is in α-axial orientation since the NMR signal of H-3 showed a small $W_{1/2}$ value. This result also confirmed that the C-4 methyl in **5b** is in α-equatorial orientation, because hydride attacked the carbonyl group from the less-hindered β-face. A similar result was also observed in the reduction of **1b**. The triol (**9a**) [mp 232—234 °C; ν_{max} 3400 cm^{-1}; δ $CDCl_3$ 3.50—3.80 (5H, m)] was obtained from the reduction of **1b** with sodium borohydride in methanol. After acetylation, the tetraacetate (**9b**) [amorphous; ν_{max} 1740 and 1715 cm^{-1}; δ $CDCl_3$ 2.02, 2.05, 2.06 and 2.09 (each 3H, s), 4.00 and 4.12 (each 1H, d, J=11.2 Hz, H-16), 4.23 (2H, m, H-15), and 4.84 (1H, br s, H-3)] was isolated. Based on above evidence, scutellone G can be assigned the structure **5b**.

Scutellone H (**2c**), needles from acetone, has the molecular formula $C_{29}H_{38}O_7$ on the basis of elementary analysis and the MS [M^+ peak at m/z 498 and fragment ion peaks at 480 ($M^+ - H_2O$), 376 ($M^+ - C_6H_5COOH$), 358 ($M^+ - H_2O - C_6H_5COOH$), 232 ($M^+ - 2H_2O - C_6H_5COOH$– ), 122 (C_6H_5COOH), and 105 (C_6H_5CO, 100%)]. The fragment ion peak at m/z 204, which corresponded to the peak at m/z 232 in **2c**, was also present in scutellone D (**2a**), scutellone E (**2b**), and scutellone F (**3**) with 67%, 100%, and 48% relative intensity, respectively.[5] The IR spectrum showed absorptions at 3450 (–OH), 1775 and 1740 (lactone), 1710 (ester), 1640 (olefin), and 1600 and 1490 cm^{-1} (benzenoid). The UV absorption of **2c** suggested the presence of an α,β,γ,δ-unsaturated γ-lactone. Our assignment of the structure of scutellone H (**2c**) was based on ^1H- and ^{13}C-NMR (Tables I and II), ^1H–^1H-COSY spectra, ^1H–^{13}C COSY spectra and the distortionless enchancement by polarization transfer (DEPT) method. Based on the above evidence, scutellone H (**2c**) must possess the same structural skeleton as scutellone D (**2a**) with the exception of an ethoxyl group in place of a hydroxyl group. The hydroxyl group located at C-3 must be in α-axial orientation, since the H-3 appears as a slightly broadened singlet at δ $CDCl_3$ 3.76. The chemical correlation of scutellone H (**2c**) to scutellone F (**3**) and scutellone E (**2b**) was achieved as follows. When scutellone F (**3**) was treated with 5% HCl in EtOH at room tempera-

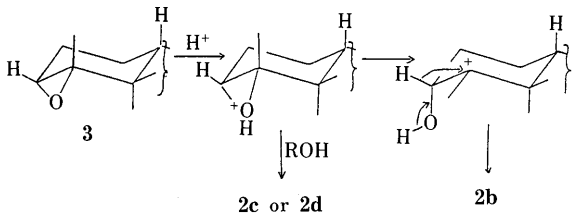

Chart 3

ture for 2 h, scutellones H (**2c**) (major) and E (**2b**) (minor) were isolated after purification. The result confirmed the structure of scutellone H (**2c**) as a new neoclerodane-type diterpenoid. The mechanism of this transformation is proposed to be as shown in Chart 3.

Scutellone I (**2d**), needles from acetone, has the molecular formula $C_{28}H_{36}O_7$ on the basis of elementary analysis. The IR spectrum showed absorption bands at 3460 (–OH), 1780, and 1745 (lactone), 1710 (ester), 1640 (olefin), and 1600 and 1490 cm^{-1} (benzenoid). The electron impact mass spectra (EIMS) exhibited the M^+ peak at *m/z* 484 and fragment ion peaks at *m/z* 362 ($M^+ - C_6H_5COOH$), 344 ($M^+ - H_2O - C_6H_5COOH$), 218 ($M^+ - 2H_2O - C_6H_5COOH$– ), 122 (C_6H_5COOH), and 105 (C_6H_5CO, 100%). The similarity of the UV absorptions of **2d** to **2a**, **2b**, **3** and **2c** suggested the presence of the same partial structure. The assignment of the structure of scutellone I (**2d**) was based on ^{1}H- and ^{13}C-NMR (Tables I and II), 2-D COSY and the DEPT method. Based on the above evidence scutellone I (**2d**) must possess the same structural skeleton as scutellone D (**2a**) with the exception of a methoxyl group in place of a hydroxyl group. The hydroxyl group located at C-3 must be in α-axial orientation, since the H-3 signal appears as a slightly broadened at δ $CDCl_3$ 3.81. When **2d** was treated with acetic anhydride in pyridine, it gave the 3-*O*-acetate (**2e**) [amorphous, δ $CDCl_3$ 2.15 (3H, s)]. The signal of H-3 was shifted downfield to δ $CDCl_3$ 4.99 (1H, br s), unambiguously suggesting that the methoxyl group is located at C-4. The relative configuration of scutellone I (**2d**) was confirmed as follows. When scutellone F (**3**) was treated with *p*-toluenesulfonic acid in methanol for 2 h at room temperature, only scutellone I (**2d**) was isolated. The mechanism of this transformation was proposed to be as shown in Chart 3. In general, for the opening of an unsymmetrical epoxide under acidic conditions, an S_N1 like reaction is more favorable. Scutellone F (**3**) is stable under neutral conditions; when refluxed in EtOH for 24 h it was recovered unchanged.

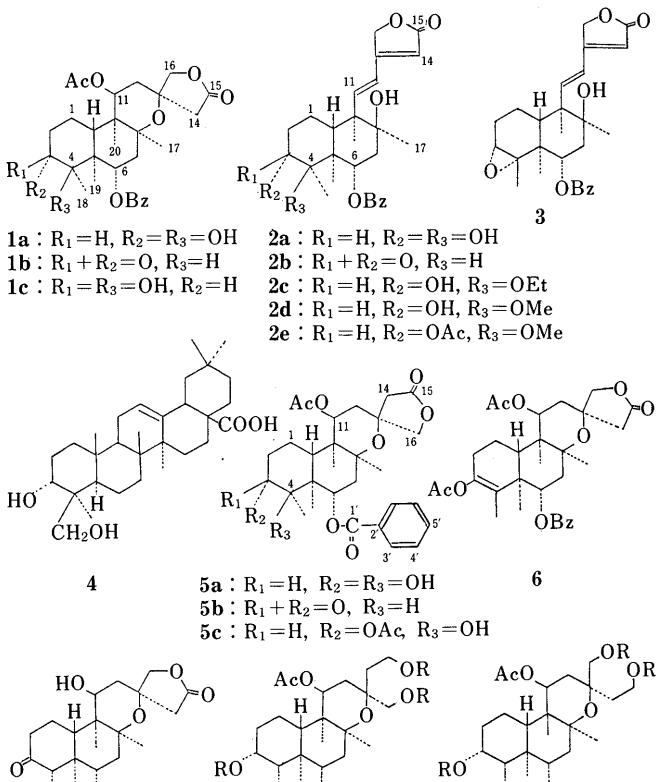

Fig. 1

Experimental

Melting points wee determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter at room temperature. IR spectra were recorded on a JASCO A-102 spectrometer. ^{1}H- and ^{13}C-NMR spectra were run on a Brucker AM 300 at 300 MHz in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ-values and coupling constants (*J*) are given in hertz (Hz). EI-MS and UV spectra were taken on a JEOL JMS-100 and Hitachi RMS-4 instruments, respectively.

Extraction and Isolation The aerial parts of *Scutellaria rivularis* (6.2 kg) was extracted with ethanol four times. The combined ethanol solution was evaporated to leave a residue, which was extracted with ether successively. The ether extract was separated by chromatography on silica gel and then on Sephadex LH-20. The purification of scutellones A, B, C, D, E, F and scutellaric acid, in addition to eighteen flavonoid constituents, was described in previous reports.[2f,h] From the mother liquid of scutellones A—F, we carried out careful separation by repeated chromatography on silica gel. Scutellone G (**5b**) (25 mg), scutellone H (**2c**) (20 mg), and scutellone I (22 mg) were isolated.

Scutellone B (1b) Colorless needles, mp 196—198 °C, $[\alpha]_D^{20}$ +54.9° (*c*= 1.0 in $CHCl_3$). UV λ_{max}^{MeOH}: 230.5, 273, 282 nm (log ε 4.12, 3.04, 2.98, respectively). *Anal.* Calcd for $C_{29}H_{36}O_8$: C, 67.95; H, 7.08. Found: C, 67.77; H, 7.10. IR ν_{max}^{KBr} cm^{-1}: 1780, 1740, 1715, 1600, 1585, 1490, 1270, 1225, 1115, 1025, 715. ^{1}H-NMR: Table I; ^{13}C-NMR: Table II.

Scutellone G (5b) Colorless needles, mp 262—263 °C. $[\alpha]_D^{24}$ +15.0° (*c*= 1.0 in $CHCl_3$). UV λ_{max}^{MeOH}: 230, 273.5, 282 nm (log ε 4.09, 3.01, 2.98, respectively). *Anal.* Calcd for $C_{29}H_{36}O_8$: C, 67.95; H, 7.08. Found: C, 68.10; H, 7.03. IR ν_{max}^{KBr} cm^{-1}: 1780, 1740, 1715, 1600, 1585, 1490, 1275, 1220, 1115, 1025, 715. ^{1}H-NMR: Table I; ^{13}C-NMR: Table II.

Scutellone H (2c) Colorless needles, mp 244—245 °C. $[\alpha]_D^{23}$ +11.1° (*c*=0.3 in $CHCl_3$), UV λ_{max}^{MeOH}: 232, 262 nm (log ε 4.20, 4.36, respectively). *Anal.* Calcd for $C_{29}H_{38}O_7$: C, 69.85; H, 7.68. Found: C, 69.36; H, 7.71. IR ν_{max}^{KBr} cm^{-1}: 3450, 3060, 1775, 1740, 1710, 1640, 1600, 1590, 1275, 1115, 1065, 1025, 715. ^{1}H-NMR: Table I; ^{13}C-NMR: Table II.

Scutellone I (2d) Colorless needles, mp 265—266 °C. $[\alpha]_D^{20}$ +8.7° (*c*= 0.4 in $CHCl_3$). UV λ_{max}^{MeOH}: 233, 262 nm (log ε 4.21, 4.37, respectively). *Anal.* Calcd for $C_{28}H_{36}O_7$: C, 69.40; H, 7.48. Found: C, 69.21; H, 7.39. IR ν_{max}^{KBr} cm^{-1}: 3460, 3040, 1780, 1745, 1710, 1690, 1640, 1600, 1490, 1280, 1115, 1065, 1025, 715. ^{1}H-NMR: Table I; ^{13}C-NMR: Table II.

Conversion of Scutellone B (1b) to the Enol Acetate (6) Scutellone B (**1b**) (15 mg) dissolved in 2 ml of isopropenyl acetate was treated with *p*-toluenesulfoic acid at room temperature overnight. The reaction mixture was poured into 30 ml of water and extracted with dichlorimethane. The dichloromethane layer was washed with 5% aqueous $NaHCO_3$ and finally with water. The organic layer was dried (Na_2SO_4), evaporated and chromatographed on silica gel to give the enol acetate (**6**) (12 mg); IR ν_{max}^{KBr} cm^{-1}: 1785, 1730, 1715, 1635, 1600, 1585, 1315, 1270, 1230, 1020, 750, 710. ^{1}H-NMR ($CDCl_3$) δ: 1.03, 1.31, 1.42, 2.05, 2.05, 2.07 (each 3H, s), 2.74, 2.81 (each 1H, d, *J*=17.0 Hz, H-14), 4.16, 4.31 (each 1H, d, *J*=

9.2 Hz, H-16), 5.31 (1H, dd, J=12.3, 4.7 Hz, H-11), 5.50 (1H, dd, J=11.2, 4.7 Hz, H-6), 7.40—7.60 (3H, m), 7.96 (2H, dd, J=7.2, 1.3 Hz).

Partial Saponification of Scutellone B (1b) to 7 Scutellone B (**1b**) (10 mg) was added to 1 ml of 5% methanolic NaOH and the mixture was kept at room temperature for 2 h, then dropped into water. Crystallization gave **7** (7 mg). IR ν_{max}^{KBr} cm^{-1}: 3480, 1775, 1710, 1600, 1580, 1270, 1175, 710. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, d, J=6.9 Hz), 1.08, 1.15, 1.25 (each 3H, s), 2.60, 2.72 (each 1H, d, J=12.0 Hz, H-14), 4.18 (1H, dd, J=10.5, 4.5 Hz, H-11), 4.29, 4.39 (each 1H, d, J=9.0 Hz, H-16), 5.35 (1H, dd, J=10.7, 4.4 Hz, H-6), 7.40—7.60 (3H, m), 7.96 (2H, dd, J=6.6, 1.3 Hz).

Acetylation of 7 to Scutellone B (2b) Compound **7** (6 mg) was treated with Ac_2O and pyridine as usual to yield scutellone B (**1b**) (7 mg).

Conversion of Scutellone A (1a) to Scutellone B (1b) Scutellone A (**1a**) (15 mg) was treated with *p*-toluenesulfonic acid (5 mg) in $CHCl_3$ (3 ml) at 50—55 °C for 2 h. The reaction mixture was subjected to silica gel chromatography to yield scutellone B (**1b**) (10 mg).

Reduction of Scutellone G (5b) with Sodium Borohydride Excess of sodium borohydride was added in small portions to a solution of scutellone G (**5b**) (23 mg) in 1 ml of MeOH and the mixture was let stand for 3 h. The reaction mixture was then poured into excess water to yield a precipitate. The precipitate was purified by silica gel chromatography to give **8a** (18 mg): IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1600, 1580, 1275, 1045, 715. ^{1}H-NMR ($CDCl_3$) δ: 1.00 (3H, d, J=7.7 Hz), 1.13, 1.25, 1.29, 2.05 (each 3H, s), 3.50—3.80 (5H, m), 5.14 (1H, dd, J=11.1, 4.5 Hz, H-11), 5.27 (1H, dd, J=10.9, 4.6 Hz, H-6), 7.30—7.60 (3H, m), 8.00 (2H, dd, J=7.2, 1.0 Hz).

Conversion of 8a to the Tetraacetate (8b) Acetic anhydride (0.5 ml) was added to the solution of the triol (**8a**) (15 mg) in 0.3 ml of pyridine. The reaction mixture was treated as usual to give the tetraactate (**8b**) (15 mg) [IR ν_{max}^{KBr} cm^{-1}: 1735, 1710, 1600, 1575, 1230, 1025, 980, 755, 715; ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, d, J=7.1 Hz), 0.93, 1.27, 1.28 (each 3H, s), 2.04, 2.05, 2.06, 2.09 (each 3H, s), 4.11 (2H, s, H-16), 4.35 (2H, m, H-15), 4.86 (1H, br s, H-3), 5.19 (1H, dd, J=11.3, 4.8 Hz, H-11), 5.42 (1H, dd, J=12.9, 4.8 Hz, H-6), 7.40—7.60 (3H, m), 7.98 (2H, dd, J=8.7, 1.3 Hz)].

Conversion of Scutellone B (1b) to the Tetraacetate (9b) Excess of sodium borohydride was added in small portions to a solution of scutellone B (**1b**) (20 mg) in 1 ml of MeOH and the mixture was let stand for 3 h. Work-up as mentioned above yielded **9a** (15 mg): IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1600, 1580, 1260, 1020, 970, 710. ^{1}H-NMR ($CDCl_3$) δ: 0.97 (3H, d, J=6.9 Hz), 1.13, 1.19, 1.32, 2.02 (each 3H, s), 3.50—3.80 (5H, m), 5.14 (1H, dd, J=11.2, 4.6 Hz, H-11), 5.28 (1H, dd, J=11.3, 4.6 Hz, H-6), 7.40—7.60 (3H, m), 7.99 (2H, dd, J=7.6, 1.2 Hz). The triol (**9a**) yielded the tetraacetate (**9b**) under usual acetylation conditions, and the spectral data of **9b** were as follows: IR ν_{max}^{KBr} cm^{-1}: 1740, 1715, 1600, 1580, 1230, 1025, 980, 715. ^{1}H-NMR ($CDCl_3$) δ: 0.98 (3H, d, J=6.7 Hz), 0.99, 1.27, 1.31, 2.02, 2.05, 2.06, 2.09 (each 3H, s), 4.00, 4.12 (each 1H, d, J=11.2 Hz, H-16), 4.23 (2H, m, H-15), 4.84 (1H, br s, H-3), 5.19 (1H, dd, J=11.2, 4.8 Hz, H-11), 5.42 (1H, dd, J=11.4, 4.6 Hz, H-6), 7.40—7.60 (3H, m), 7.99 (2H, dd, J=8.1, 1.0 Hz).

Conversion of Scutellone F (3) to Scutellones H (2c) and E (2b) Scutellone F (**3**) (32 mg) was treated with 1 ml of 5% ethanolic HCl at room temperature for 2 h, then the reaction mixture was poured into excess water and worked up as usual. The purification was performed by silica gel chromatography, and gave scutellones H (**2c**) (21 mg) and E (**2b**) (5 mg).

Acetylation of Scutellone I (2d) Acetic anhydride (0.4 ml) was added to a solution of scutellone I (**2d**) (15 mg) in 0.4 ml of pyridine at room temperature overnight. The reaction mixture was treated as usual to give the monoacetate (**2e**) (14 mg). [IR ν_{max}^{KBr} cm^{-1}: 3400, 1775, 1745, 1715, 1645, 1600, 1375,1115, 1065, 1025, 715; ^{1}H-NMR ($CDCl_3$) δ: 1.03, 1.10, 1.11, 1.42, 2.04, 3.25 (each 3H, s), 4.99 (2H, br s, H-3, H-14), 5.98 (1H, dd, J=11.9, 5.6 Hz), 6.36 (2H, s, H-11, H-12), 7.40—7.60 (3H, m), 7.99 (2H, dd, J=7.2, 1.2 Hz)].

Conversion of Scutellone F (3) to Scutellone I (2d) Scutellone F (**3**) (21 mg) was treated with *p*-toluenesulfonic acid (5 mg) in methanol (3 ml) at room temperature for 2 h. The reaction mixture was subjected to silica gel chromatography, providing scutellone I (**2d**) (15 mg).

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