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FLAVONOID COMPOUNDS IN ROOTS OF *SOPHORA TETRAPTERA*

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Key Word Index—*Sophora tetraptera*; Leguminosae; roots; flavonoids; isoflavanone; pterocarpan; tetrapterol.

Abstract—Two novel flavonoid compounds, an isoflavanone, tetrapterol A, and a pterocarpan, tetrapterol B, and three new isoflavanones, tetrapterols C–E, were isolated from the roots of *Sophora tetraptera*, in addition to eight known phenolic compounds (kenusanone A, lespedeol B, euchenone a_9, lonchocarpol A, cajanone, (−)-maackiain, isoneorautenol and pentacosanyl caffeate). The two novel compounds had a common characteristic partial structure which is derived from a geranyl group which forms a new aromatic ring after cyclization with a hydroxyl group located at a side ring in a flavonoid framework and dehydrogenation. The new isoflavanones had a geranyl or an isoprenyl group on their A or B ring. The structures were determined by analysis of spectral data, in particular, 2D-NMR.

INTRODUCTION

Sophora tetraptera, native to New Zealand, is classified into subgenus Sophora, section Sophora, series Tetrapterae, by Tsoong and Ma [1]. By previous examination of *S. tetraptera*, the presence of matrine-type quinolizidine alkaloids from the seeds [2] and apigenin glycosides from the leaves [3] has been revealed. A precise investigation directed to phenolic compounds and to phytochemical relationships with other *Sophora* species resulted in isolation of 13 flavonoid compounds from the roots of *S. tetraptera*. In the present paper, we describe the isolation and structural determination of these compounds.

RESULTS AND DISCUSSION

An acetone extract of the roots of *S. tetraptera* was subjected to vacuum liquid column chromatography (VLC) on silica gel 60H eluting with a *n*-hexane–acetone system. Further purification of the fractions was carried out by VLC, Sephadex LH-20 column chromatography and preparative TLC to give 13 phenolic compounds.

Tetrapterol A (**1**) [4], obtained as a colourless oil, showed a $[M]^+$ at *m/z* 418 in the EI-mass spectrum corresponding to the empirical formula, $C_{25}H_{22}O_6$. In the ^1H NMR spectrum, two one-proton double doublets [δ4.75 and 4.94 (J = 12, 5 Hz)] and a one-proton triplet [δ4.07 (J = 5 Hz)], which were assignable to H-2 and H-3 in an isoflavanone skeleton, were observed. Proton signals at δ5.98, 6.03 (1H each, *d*, J = 1 Hz) and 11.80 (1H, *s*, chelated OH) in the spectrum and the fragment ions at *m/z* 153 (**1a**) and 152 (**1a** − H) in the EI-mass spectrum (Fig. 1) caused by retro-Diels–Alder cleavage, indicated that the A-ring moiety had a 5,7-dihydroxyl substitution. Three methyl groups [δ1.57, 1.60 (O–C(Me)$_2$) and 2.39 (attached to an aromatic ring)], three aromatic protons in a ABM spin system [δ7.04 (*br d*, J = 8 Hz), 7.09 (*d*, J = 8 Hz) and 7.39 (*br s*)] and two aromatic protons in a singlet (δ6.53 and 7.74) were attributable to the B-ring. In the difference NOE (DIFNOE) spectrum (Fig. 2), irradiation of the benzylmethyl protons (δ2.39) enhanced the aromatic protons (δ7.04 and 7.39), the latter of which showed a NOE enhancement with the aromatic singlet (δ7.74). Therefore, the structure of the B-ring moiety could be depicted as in Fig. 2. The COLOC spectrum (Fig. 3) supported the structure of tetrapterol A as **1**.

Tetrapterol B (**2**) [4], obtained as a colourless oil, showed a $[M]^+$ at *m/z* 386 in the EI-mass spectrum which corresponds to $C_{25}H_{22}O_4$. The UV absorption bands and a set of four protons [δ3.60 (*m*), 3.68 (*t*, J = 11 Hz), 4.31 (*dd*, J = 11, 5 Hz) and 5.51 (*d*, J = 7 Hz)] in the ^1H NMR spectrum indicated that **2** was a pterocarpan derivative. The ^1H and ^{13}C NMR spectra also showed the presence of the same partial structure based on a geranyl unit as described in **1**. Three protons in an ABX spin system [δ6.43 (*d*, J = 2 Hz), 6.55 (*dd*, J = 9, 2 Hz), 7.41 (*d*, J = 9 Hz)], two singlet aromatic protons (δ6.45 and 7.59) and a hydroxyl signal (δ4.85) were insufficient to determine the location of the moiety, whether it was substituted on the A- or D-ring of a demethylmedicarpin (3,9-dihydroxypterocarpan), because of the equivalent substitution between two rings (a homospecific flavonoid) [5]. In the DIFNOE spectrum (Fig. 4), an NOE interaction was observed between an

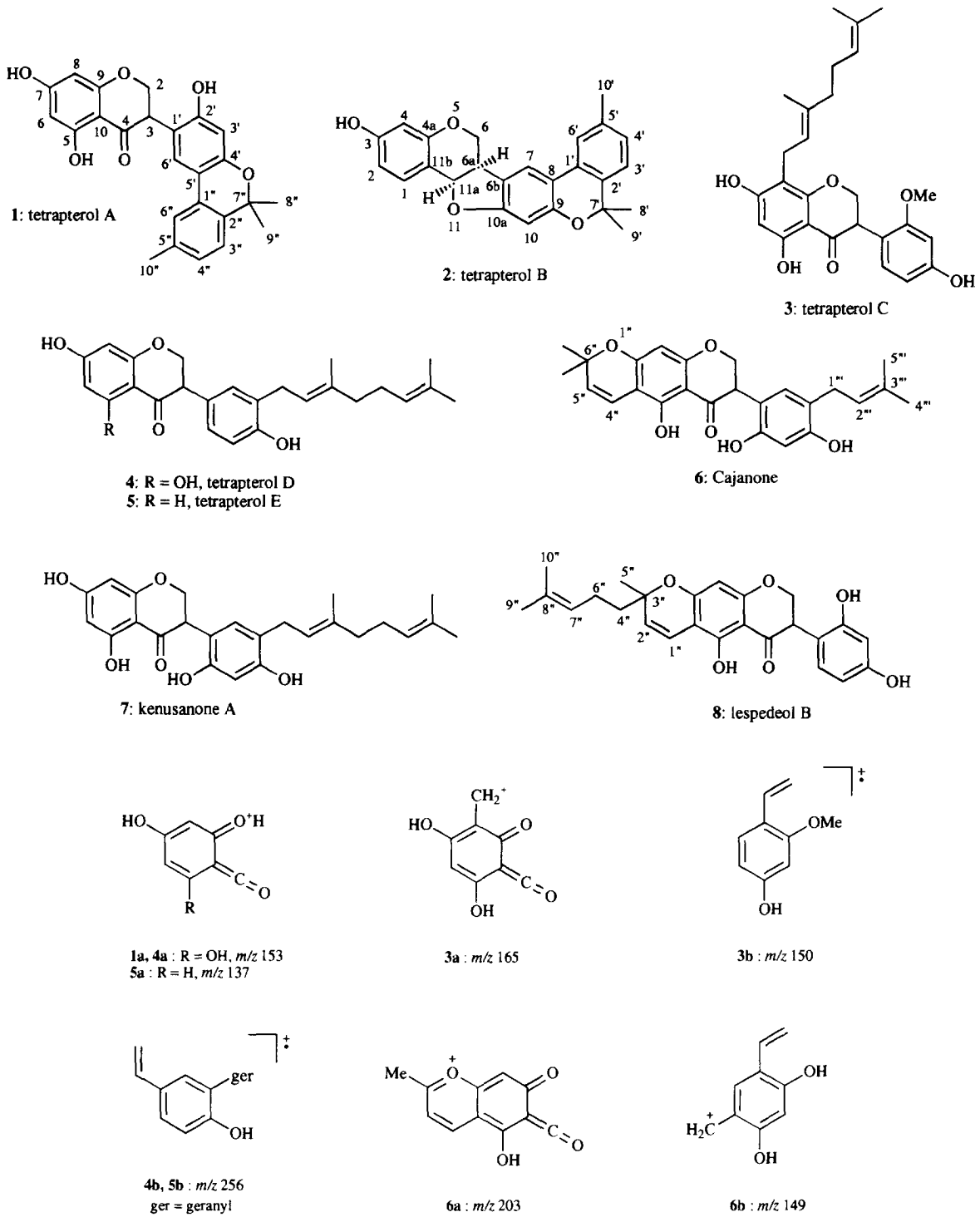

Fig. 1. Fragment ions in the EI mass spectrum of **1**–**6**.

aromatic doublet (δ7.41) assignable to H-1 and an oxymethine doublet (δ5.51) assignable to H-11a, indicating that the moiety was located on the D-ring. The structure for tetrapterol B was substantiated with the aid of DIFNOE and HMBC spectra as **2** (Fig. 5). The value of the specific rotation ($[\alpha]_D$ − 236°) indicated that the absolute configuration of C-6a and C-11a was *R* in each case [6, 7].

Tetrapterol C (**3**), a pale yellow oil, showed a $[M]^+$ at *m/z* 438, corresponding to an empirical formula of $C_{26}H_{30}O_6$. The ^{1}H NMR spectrum exhibited a set of three methine protons at 4.26 (*dd*, *J* = 11, 6 Hz), 4.47

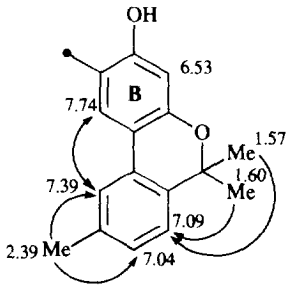

Fig. 2. NOE interactions in the DIFNOE spectrum of **1**.

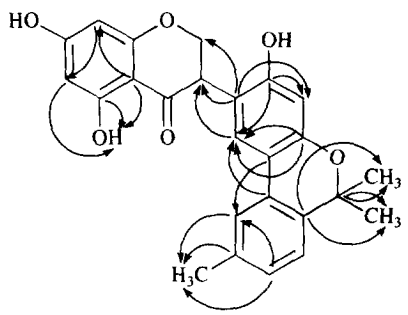

Fig. 3. Long range correlations in the COLOC spectrum (J = 10 Hz) of **1**.

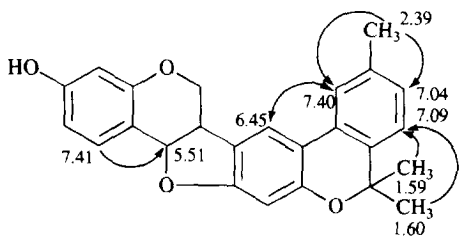

Fig. 4. NOE interactions in the DIFNOE spectrum of **2**.

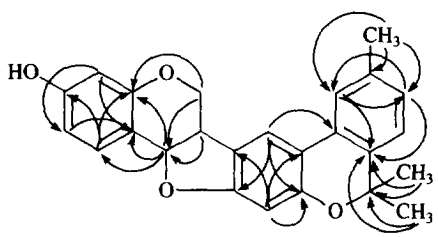

Fig. 5. Long range correlations in the HNBC spectrum (J = 10 Hz) of **2**.

(*dd*, J = 11, 6 Hz) and 4.53 (*t*, J = 11 Hz), which were assigned to H-3 and H-2 in an isoflavanone skeleton. The spectrum also showed the presence of a geranyl (or neryl) group [δ1.56, 1.62, 1.75 (3H each, *br s*, vinylic Me), 1.96 (4H, *m*, CH_2CH_2), 3.25 (2H, *d*, J = 6 Hz, CH_2), 5.08 and 5.22 (1H each, *t*-like *m*, CH=)], as well as a methoxyl group (δ3.76) and three hydroxyl groups [δ8.41, 9.55 (1H each, *br s*, OH) and 12.34 (1H, *s*, chelated OH)]. The carbon signals at δ40.4 and 16.1 assignable to C-4″ and C-5″ in the ^{13}C NMR spectrum indicated that the C_{10} unit is not a neryl, but a geranyl group [8]. A fragment ion at m/z 165 (**3a**) in the EI-mass spectrum and a one-proton aromatic singlet at δ6.04 in the ^{1}H NMR spectrum indicated that the A-ring had 8 (or 6)-geranyl-5,7-dihydroxyl substitution. The location of the geranyl group was determined by comparison of the chemical shift based on the chelated hydroxyl group of **3** (δ12.34) with that of kenusanone H (8-geranyl-5,7,2′,4′-tetrahydroxyisoflavanone) (δ12.33) [9]. The fragment ion at m/z 150 (**3b**) in the EI-mass spectrum and three aromatic protons [δ6.41 (*dd*, J = 8, 2 Hz), 6.52 (*d*, J = 2 Hz) and 6.98 (*d*, J = 8 Hz)] in an ABX system suggested that the B-ring bore a methoxyl and a hydroxyl group at C-2′ and C-4′. The enhancement of H-3′ (δ6.52) on irradiation of the methoxyl group in the DIFNOE spectrum showed that the methoxyl group was located at C-2′ and the hydroxyl group at C-4′ as a natural consequence. The structure of tetrapterol C was concluded to be 8-geranyl-5,7,4′-trihydroxy-2′-methoxyisoflavanone (**3**) (kenusanone H 2′-methyl ether).

Tetrapterol D (**4**), a pale yellow oil, gave a $[M]^+$ at m/z 408 for $C_{25}H_{28}O_5$ in the EI-mass spectrum and was an isoflavanone. The ^{1}H NMR spectrum showed the presence of a geranyl group and a chelated hydroxyl group (δ12.26). As two aromatic protons at δ5.92 and 5.95 were assigned to H-6 and H-8, the A-ring had a 5,7-dihydroxyl substitution. Fragment ions at m/z 153 (**4a**) and 256 (**4b**) due to retro-Diels–Alder cleavage in the EI-mass spectrum substantiated such an oxygenation pattern of the A-ring and supported that the B-ring had a hydroxyl group and a geranyl group. Three protons appearing as an ABX spin system [δ6.82 (*d*, J = 8 Hz), 6.97 (*dd*, J = 8, 2 Hz) and 7.06 (*d*, J = 2 Hz)] were assigned to H-5′, H-6′ and H-2′, respectively, indicating that the B-ring had a 3′-geranyl-4′-hydroxyl substitution. The structure of tetrapterol D was then concluded to be 3′-geranyl-5,7,4′-trihydroxyisoflavanone (**4**).

Tetrapterol E (**5**), a yellow oil, showed $[M]^+$ at m/z 392 for its empirical formula of $C_{25}H_{28}O_4$ in the EI-mass spectrum. The ^{1}H NMR spectral data of the B-ring moiety were closely compatible with those of **4**. Fragment ions observed at m/z 256 (**5b**), 187 (**5b** $-C_5H_9$) and 133 (**5b** $-C_9H_{15}$) demonstrated that the B-ring had a 3′-geranyl-4′-hydroxyl substitution. Three aromatic protons at δ6.40 (1H, *d*, J = 2 Hz), 6.57 (1H, *dd*, J = 9,2 Hz) and 7.74 (1H, *d*, J = 9 Hz) were reasonably assigned to H-8, H-6 and H-5 of the isoflavanone, indicating that the A-ring possessed a 7-hydroxyl substitution. Consequently, the structure of tetrapterol E was characterized as 3′-geranyl-7,4′-dihydroxyisoflavanone (**5**).

Cajanone (**6**), [10] a pale yellow oil, was an isoflavanone with the molecular formula $C_{25}H_{26}O_6$ ($[M]^+$ m/z 422). In the ^{1}H NMR spectrum, three aromatic protons, each as singlets, were observed at δ5.87, 6.47 and 6.82. The spectrum also exhibited the presence of a γ,γ-dimethylallyl group [δ1.63, 1.66 (3H each, *br s*, Me × 2), 3.19 (2H, *d*,

$J = 7$ Hz, CH_2) and 5.26 (1H, *t*-like *m*, CH=)] and a 6,6-dimethylpyran ring [δ1.44 (6H, *s*, Me×2), 5.62 (1H, *d*, $J = 10$ Hz, CH=) and 6.58 (1H, *d*, $J = 10$ Hz, CH=)]. A fragment ion at *m/z* 149 (**6b**) in the EI-mass spectrum and two aromatic singlets at δ6.47 and 6.82 in the ^{1}H NMR spectrum, indicated that two hydroxyls and the γ,γ-dimethylallyl group were located at C-2′, C-4′ and C-5′, respectively, on the B-ring. A fragment ion at *m/z* 203 (**6a**) supported that the dimethylpyran ring and a hydroxyl group were on the A-ring. The fusion of the dimethylpyran ring and the A-ring was in a linear form because a chelated hydroxyl group was observed at δ12.75. The structure of cajanone was thus concluded to be 5′-γ,γ-dimethylallyl-[7,6:2″,3″]-6″,6″-dimethylpyrano-5,2′,4′-trihydroxyisoflavanone.

In addition to the five new compounds described above, seven known phenolic constituents were also isolated and characterized by spectral evidence as follows: two isoflavanones; kenusanone A (**7**) [11] and lespedeol B (**8**) [12], two flavanones; lonchocalpol A (**9**) [13] and euchrenone a_9 (**10**) [14], two pterocarpans; (−)-maackiain (**11**) and isoneorautenol (**12**) [15], and a phenyl propanoid; pentacosanyl caffeate (**13**).

The structure of tetrapterol A (**1**) is closely correlated to that of kenusanone A (5′-geranyl-5,7,2′,4′-tetrahydroxyisoflavanone) (**7**) because the geranyl group is cyclized with the hydroxyl group at C-4′ through an *exo*-methine in the geranyl group and dehydrogenated to form a new aromatic ring to finally produce tetrapterol A (**1**). This route also applies to tetrapterol B (**2**), but its precursor (8-geranyl-demethylmedicarpin) was not detected in the roots in the present experiments. The biosynthetic pathway of ring formation is considered to be identical to that of cannabinol in *Cannabis sativa*. On the other hand, this species has another enzyme that contributes to cyclization of a geranyl with an *ortho*-substituted hydroxyl group through an *endo*-methine of the group, as found in lespedeol B (**8**). The occurrence of tetrapterols A and B discriminates this species from other *Sophora* species (*S. koreensis*, *S. tomentosa* and *S. chrysophylla*) which also contain flavonoids with a geranyl group by the formation of an aromatized ring.

EXPERIMENTAL

Plant material. Roots of *S. tetraptera* J. S. Mill were collected at the nursery of Landcare Research New Zealand Ltd in June 1993. Voucher specimens are deposited in the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation. Dried and pulverized roots (125 g) were extracted with Me_2CO at room temp. After concn of solvent, the extract (6.4 g) was subjected to VLC on silica gel 60H (Merck) with *n*-hexane–Me_2CO (20:1 to 1:1) to obtain 11 frs. Further purification by VLC (*n*-hexane–EtOH system), Sephadex LH-20 CC (MeOH) and prep. TLC ($CHCl_3$–MeOH system) gave two compounds [**2** (3 mg), **13** (10 mg)] from the (10:1) eluate, and 11 compounds [**1** (8 mg), **3** (6 mg), **4** (25 mg), **5** (12 mg), **6** (3 mg), **7** (20 mg), **8** (1 mg), **9** (15 mg), **10** (2 mg), **11** (1 mg), **12** (6 mg)] from the (8:1) eluate.

Tetrapterol A (**1**). Colourless oil. EIMS *m/z* (rel. int.): 418 $[M]^+$ (46), 403 (100), 277 (20), 251 (41), 249 (9), 153 (5), 152 (4). $[\alpha]_D^{25}$ −8.4° (MeOH; *c* 0.17). UV λ_{max} (MeOH, nm): 219, 283, 295sh, 315, 325 sh. ^{1}H and ^{13}C NMR: see Table 1.

Tetrapterol B (**2**). Colourless oil. EIMS *m/z* (rel. int.): 386 $[M]^+$ (53), 371 (100), 307 (7), 185 (13), 149 (7). $[\alpha]_D^{25}$ −236.2° (MeOH; *c* = 0.05). UV λ_{max} (MeOH, nm): 217, 281, 298sh, 323. ^{1}H and ^{13}C NMR: see Table 1.

Tetrapterol C (**3**). Pale yellow oil. EIMS *m/z* (rel. int.): 438 $[M]^+$ (47), 369 (39), 315 (100), 165 (72), 150 (47). UV λ_{max} (MeOH, nm): 207, 224sh, 289 320 sh. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.56, 1.62, 1.75 (3H each, *br s*, Me), 1.96 (4H, *m*, H-4″, H-6″), 3.25 (2H, *d*, $J = 6$ Hz, H-1″), 3.76 (3H, *s*, OMe), 4.26 (1H, *dd*, $J = 11$, 6 Hz, H-3), 4.47 (1H, *dd*, $J = 11$, 6 Hz, H-2eq), 4.53 (1H, *t*, $J = 11$ Hz, H-2ax), 5.08 (1H, *t*-like *m*, H-7″), 5.22 (1H, *t*-like *m*, H-2″), 6.04 (1H, *s*, H-6), 6.41 (1H, *dd*, $J = 8$, 2 Hz, H-5′), 6.52 (1H, *d*, $J = 2$ Hz, H-3′), 6.98 (1H, *d*, $J = 8$ Hz, H-6′), 8.41, 9.55 (1H each, *br s*, OH), 12.34 (1H, *s*, C-5-OH). ^{13}C NMR (100 MHz, acetone-d_6): δ71.3 (C-2), 47.2 (C-3), 198.7 (C-4), 164.6 (C-5), 96.5 (C-6), 165.7 (C-7), 108.1 (C-8), 163.3 (C-9), 103.7 (C-10), 115.4 (C-1′), 159.2 (C-2′), 100.3 (C-3′), 159.5 (C-4′), 108.0 (C-5′), 131.7 (C-6′), 22.0 (C-1″), 123.7 (C-2″), 134.9 (C-3″), 40.4 (C-4″), 16.1 (C-5″), 27.4 (C-6″), 125.1 (C-7″), 131.8 (C-8″), 25.8 (C-9″), 17.7 (C-10″), 55.9 (OMe).

Tetrapterol D (**4**). Pale yellow oil. EIMS *m/z* (rel. int.): 408 $[M]^+$ (65), 393 (8), 339 (55), 286 (22), 285 (25), 256 (21), 188 (26), 187 (15), 153 (100), 133 (22), 123 (53). $[\alpha]_D^{25}$ −1.3° (MeOH; *c* 0.45). UV λ_{max} (MeOH, nm); 225, 289, 330 sh. ^{1}H NMR (400 MHz, acetone-d_6): δ1.58, 1.64, 1.68 (3H each, *br s*, Me), 2.06, 2.07 (2H each, *m*, H-4″, H-6″), 3.29 (2H, *d*, $J = 7$ Hz, H-1″), 3.88 (1H, *dd*, $J = 7$, 5 Hz, H-3), 4.57 (2H, *m*, H-2), 5.12 (1H, *t*-like *m*, H-7″), 5.34 (1H, *t*-like *m*, H-2″), 5.94 (1H, *d*, $J = 2$ Hz, H-6), 5.95 (1H, *d*, $J = 2$ Hz, H-8), 6.82 (1H, *d*, $J = 8$ Hz, H-5′), 6.97 (1H, *dd*, $J = 8$, 2 Hz, H-6′), 7.06 (1H, *d*, $J = 2$ Hz, H-2′), 12.26 (1H, *s*, C-5-OH). ^{1}H NMR (400 MHz, $CDCl_3$): δ1.59, 1.67, 1.73 (3H each, *br s*, Me), 2.07 (4H, *m*, H-4″, H-6″), 3.31 (2H, *d*, $J = 7$ Hz, H-1″), 3.86 (1H, *dd*, $J = 9$, 5 Hz, H-3), 4.48 (1H, *dd*, $J = 11$, 9 Hz, H-2eq), 4.54 (1H, *dd*, $J = 11$, 5 Hz, H-2ax), 5.06 (1H, *t*-like *m*, H-7″), 5.28 (1H, *t*, *H*, $J = 7$ Hz, H-2″), 5.92 (1H, *br s*, H-6), 5.95 (1H, *br s*, H-8), 6.75 (1H, *d*, $J = 9$ Hz, H-5′), 6.97–6.98 (2H, *m*, H-2′, H-6′), 12.15 (1H, *s*, C-5-OH). ^{13}C NMR (100 MHz, acetone-d_6): δ72.2 (C-2), 51.0 (C-3), 197.8 (C-4), 165.7 (C-5), 96.9 (C-6), 167.3 (C-7), 95.5 (C-8), 164.2 (C-9), 103.2 (C-10), 127.5 (C-1′), 127.6 (C-2′), 128.9 (C-3′), 155.3 (C-4′), 115.8 (C-5′), 130.6 (C-6′), 28.8 (C-1″), 123.2 (C-2″), 136.5 (C-3″), 40.4 (C-4″), 16.2 (C-5″), 27.4 (C-6″), 125.1 (C-7″), 131.7 (C-8″), 25.8 (C-9″), 17.7 (C-10″).

Tetrapterol E (**5**). Pale yellow oil. EIMS *m/z* (rel. int.): 392 $[M]^+$ (62), 323 (13), 270 (37), 269 (14), 256 (37), 188 (28), 187 (10), 137 (100), 133 (26), 123 (40). $[\alpha]_D^{25}$ +19.4° (MeOH; *c* = 0.39). UV λ_{max} (MeOH, nm): 207, 225sh, 279, 305sh. ^{1}H NMR (400 MHz, acetone-d_6): δ1.58, 1.64, 1.68 (3H each, *br s*, Me), 2.04 (4H, *m*, H-4″, H-6″), 3.30 (2H, *d*,

Table 1. ^1H and ^{13}C NMR spectral data of compounds **1** and **2** in $CDCl_3$

	1			**2**	
C	δ_H	δ_C	C	δ_H	δ_C
2	4.75 (*dd*, 12, 5)	69.7	1	7.41 (*d*, 9)	132.3
	4.94 (*dd*, 12, 5)		2	6.55 (*dd*, 9, 2)	109.8
3	4.07 (*t*, 5)	45.6	3		157.0
4		196.9	4	6.43 (*d*, 2)	103.7
5		165.0	4a		156.7
6	5.98 (*d*, 1)	97.0	6	3.68 (*t*, 11)	66.7
7		166.0		4.31 (*dd*, 11, 5)	
8	6.03 (*d*, 1)	95.6	6a	3.60 (*m*)	39.7
9		163.3	6b		120.5
10		102.0	7	7.59 (*s*)	118.7
1′		115.6	8		115.7
2′		153.3	9		154.5
3′	6.53 (*s*)	106.7	10	6.45 (*s*)	100.4
4′		156.0	10a		160.0
5′		116.2	11a	5.51 (*d*, 7)	78.4
6′	7.74 (*s*)	122.4	11b		112.7
1″		128.1	1′		128.7
2″		135.7	2′		135.5
3″	7.09 (*d*, 8)	123.1	3′	7.09 (*d*, 7)	123.1
4″	7.04 (*br d*, 8)	127.9	4′	7.04 (*br d*, 7)	127.7
5″		137.2	5′		137.2
6″	7.39 (*br s*)	122.0	6′	7.40 (*br d*, 2)	121.9
7″		78.1	7′		78.1
8″, 9″	1.57 (*s*)	27.7	8′,9′	1.59 (*s*)	27.7
	1.60 (*s*)	27.6		1.60 (*s*)	27.7
10″	2.39 (*br s*)	21.3	10′	2.39 (*br s*)	21.3
OH	4.10 (*br s*)		OH	4.85 (*br s*)	
	11.80 (*s*)				

Values are in ppm (δ_H and δ_C). ^1H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively. Figures in parentheses are coupling constants (J) in Hz.

J = 7 Hz, H-1″), 3.80 (1H, *t*, J = 6 Hz, H-3), 4.60 (2H, *d*, J = 6 Hz, H-2), 5.11 (1H, *t*-like *m*, H-7″), 5.34 (1H, *t*-like *m*, H-2″), 6.40 (1H, *d*, J = 2 Hz, H-8), 6.57 (1H, *dd*, J = 9, 2 Hz, H-6), 6.77 (1H, *d*, J = 8 Hz, H-5′), 6.94 (1H, *dd*, J = 8, 2 Hz, H-6′), 7.04 (1H, *d*, J = 2 Hz, H-2′), 7.74 (1H, *d*, J = 9 Hz, H-5). ^1H NMR (400 MHZ, $CDCl_3$): δ1.58, 1.66, 1.72 (3H each, *br s*, Me), 2.05 (4H, *m*, H-4″, H-6″), 3.29 (2H, *d*, J = 7 Hz, H-1″), 3.84 (1H, *dd*, J = 9, 5 Hz, H-3), 4.53 (1H, *dd*, J = 11, 9 Hz, H-2eq), 4.59 (1H, *dd*, J = 11, 5 Hz, H-2ax), 5.05 (1H, *t*-like *m*, H-7″), 5.28 (1H, *t*-like *m*, H-2″), 6.38 (1H, *d*, J = 2 Hz, H-8), 6.47 (1H, *dd*, J = 9, 2 Hz, H-6), 6.72 (1H, *d*, J = 8 Hz, H-5′), 6.95–6.97 (2H, *m*, H-2′, H-6′), 7.82 (1H, *d*, J = 9 Hz, H-5). ^{13}C NMR (100 MHz, acetone-d_6): δ72.7 (C-2), 51.9 (C-3), 191.1 (C-4), 130.1 (C-5), 111.3 (C-6), 165.0 (C-7), 103.3 (C-8), 164.3 (C-9), 115.3 (C-10), 128.0 (C-1′), 127.6 (C-2′), 128.7 (C-3′), 155.0 (C-4′), 115.7 (C-5′), 130.6 (C-6′), 28.8 (C-1″), 123.3 (C-2″), 136.4 (C-3″), 40.4 (C-4″), 16.2 (C-5″), 27.4 (C-6″), 125.1 (C-7″), 131.6 (C-8″), 25.8 (C-9″), 17.7 (C-10″).

Cajanone (**6**). Pale yellow oil. EIMS *m/z* (rel. int.): 422 $[M]^+$ (100), 389 (51), 285 (8), 233 (10), 219 (17), 218 (13), 217 (53), 203 (36), 176 (21), 149 (22). $[\alpha]_D^{25}$ + 3.9° (MeOH; *c* 0.10). UV λ_{max} (MeOH, nm): 213, 218sh, 272, 292, 305sh, 340sh. ^1H NMR (400 MHz, acetone-d_6): δ1.44 (6H, *s*, Me), 1.63, 1.66 (3H each, *br s*, Me), 3.19 (2H, *d*, J = 7 Hz, H-1″), 4.22 (1H, *dd*, J = 10, 5 Hz, H-3), 4.47 (1H, *dd*, J = 11, 5 Hz, H-2eq), 4.62 (1H, *dd*, J = 11, 10 Hz, H-2ax), 5.26 (1H, *t*-like *m*, H-2″), 5.62 (1H, *d*, J = 10 Hz, H-5″), 5.87 (1H, *s*, H-8), 6.47 (1H, *s*, H-3′), 6.58 (1H, *d*, J = 10 Hz, H-4″), 6.82 (1H, *s*, H-6′), 8.08, 8.21 (1H each, *br s*, OH), 12.75 (1H, *s*, C-5-OH).

Lespedeol B (**8**). Pale yellow oil. EIMS *m/z* (rel. int.): 422 $[M]^+$ (22), 407 (6), 339 (100), 287 (4), 245 (8), 217 (25), 203 (17), 149 (5), 136 (6). UV λ_{max} (MeOH, nm): 207, 226, 273, 295, 310, 353. ^1H NMR (400 MHz, acetone-d_6): δ1.42, 1.57, 1.65 (3H each, *br s*, Me), 1.73, 2.06 (2H each, *m*, H-4″, H-6″), 4.27 (1H, *dd*, J = 11, 5 Hz, H-3), 4.47 (1H, *dd*, J = 11, 5 Hz, H-2eq), 4.62 (1H, *t*, J = 11 Hz, H-2ax), 5.12 (1H, *t*-like *m*, H-7″), 5.59 (1H, *d*, J = 10 Hz, H-2″), 5.88 (1H, *s*, H-8), 6.34 (1H, *dd*, J = 8, 3 Hz, H-5′), 6.44 (1H, *d*, J = 3 Hz, H-3′), 6.63 (1H, *d*, J = 10 Hz, H-1″), 6.95 (1H, *d*, J = 8 Hz, H-6′), 8.23, 8.55 (1H each, *br s*, OH), 12.73 (1H, *s*, C-5-OH).

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