PERGAMON

Phytochemistry 50 (1999) 695–701

PHYTOCHEMISTRY

Four isoflavanones from roots of *Sophora tetraptera*[1]

Yoshiaki Shirataki[a,*], Satoko Matsuoka[a], Manki Komatsu[a], Masayoshi Ohyama[b], Toshiyuki Tanaka[b], Munekazu Iinuma[b]

[a]*Faculty of Pharmaceutical Sciences, Josai University, 1-1 Keyakidai Sakado, Saitama, 350-02 Japan.*
[b]*Department of Pharmacognosy, Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5 chome, Gifu, 502, Japan.*

Revised 14 April 1998

Abstract

Four new isoflavanones, tetrapterols F–I, were isolated from roots of *Sophora tetraptera* in addition to seven known flavonoids, lupinifolin, 8-*O*-methylretusin, 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone, (−)-maackiain, sophoracarpan A, medicagol and 2-(2,4-dihydroxyphenyl)-5,6-methylenedioxybenzofuran. The structure of the new isoflavanones was determined to be 3,5,7–trihydroxy-2′-methoxy-8-γ,γ-dimethylallyl-6‴,6‴-dimethylpyrano[2‴,3‴:4′,3′]isoflavanone(tetrapterol F), 5,7,2′,4′-tetrahydroxy-6,5′-di(γ,γ-dimethylallyl)isoflavanone(tetrapterol G), 5,7,2′–trihydroxy–4′–methoxy-8,5′-di(γ,γ-dimethylallyl)-isoflavanone(tetrapterol H) and 7,4′-dihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavanone (tetrapterol I) by means of spectroscopic analysis.

Keywords: *Sophora tetraptera*; Leguminosae; 3–Hydroxyisoflavanone; Isoflavanone; Tetrapterols F–I

1. Introduction

In previous papers, we have reported the isolation and structural elucidation of 13 phenolic compounds including five new flavonoids, tetrapterols A–E, from roots of *Sophora tetraptera* J.S. Mill (Tanaka, Ohyama, Kawasaka & Iinuma, 1994; Iinuma, Ohyama, Kawasaka & Tanaka, 1995). The occurrence of tetrapterols A and B which have an additional aromatic ring formed by cyclization and successive dehydrogenation of a geranyl group in a flavonoid skeleton distinguishes this plant from other *Sophora* species. Further study of the root constituents led to the isolation of four new isoflavanones, named tetrapterols F(**1**)–I(**4**), from the ether soluble fraction. This paper deals with the structural elucidation of these compounds.

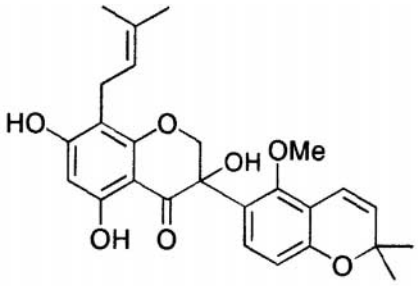
2. Results and discussion

Compound **1**, was isolated from a methanolic root extract of *S. tetraptera*, (see Section 3) as a yellow oil and gave a $[M]^+$ at *m*/*z* 452 in the EI-mass spectrum corresponding to the empirical formula $C_{26}H_{28}O_7$. The ^1H NMR spectrum showed two one-proton doublets at δ 4.20 and 4.71 (each $J = 12.0$ Hz) which were assignable either to H-3 and H-2 in a flavanonol skeleton or to H-2 in a 3–hydroxyisoflavanone skeleton. Since these two protons were correlated with a carbon signal at δ 75.5 tentatively assigned to C-2 in the ^{13}C–^1H COSY spectrum, they could be allotted to hydrogens at C-2, which suggested that **1** was a 3–hydroxyisoflavanone derivative. In the ^1H NMR spectrum, the presence of three hydroxyl groups [δ 5.55, 9.58 and 12.08 (chelated)], a methoxyl group (*d* 3.63), a γ,γ-dimethylallyl group [δ 1.63, 1.72 (3H each, *s*, Me×2), 3.23 (2H, *t* like *m*, CH_2), 5.21 (1H, *t* like *m*, CH=)] and a dimethylchromene ring [δ 1.39, 1.45 (3H each, *s*, Me×2), 5.78, 6.53 (1H each, *d*, $J = 10.0$ Hz, *cis*-olefinic proton)] were distinguished as well as a one-proton aromatic singlet (*d* 6.08) and a set of *ortho*-coupled

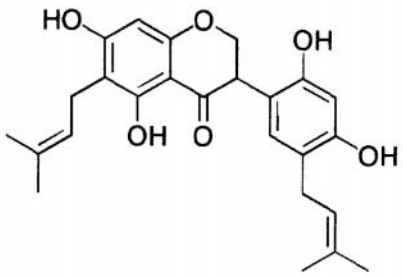
* Corresponding author.

[1] Part 26 in the series 'Studies on the Constituents of *Sophora* Species'. For Part 25 see Shirataki, Y., Yoshida, S., Sugita, Y., Yokoe, I., Komatsu, M., Ohyama, M., Tanaka, T., & Iinuma, M. (1997) *Phytochemistry, 44*, 715.

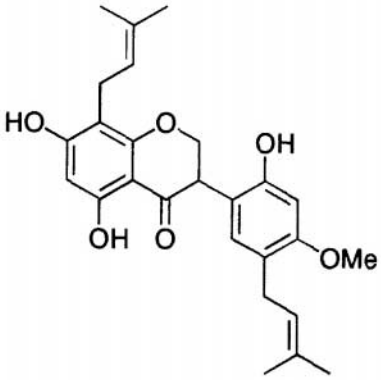
0031-9422/98 $ - see front matter
PII: S0031-9422(98)00551-2



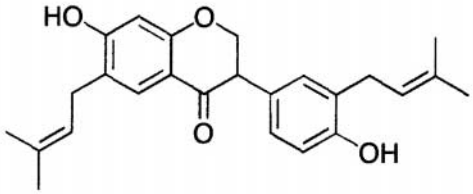
tetrapterol F (**1**)



tetrapterol G (**2**)



tetrapterol H (**3**)



tetrapterol I (**4**)

aromatic doublets [δ 6.60, 7.46 (1H each, *d*, $J = 8.5$ Hz)]. Significant fragments at *m/z* 221 $[A_1 + H]^+$ (**1a**), 165 $[A_1 - C_4H_7]^+$ (**1b**) and 217 $[B_1 - CH_3]^+$ (**1c**) based on *retro*-Diels–Alder fragmentation in the EIMS (Fig. 1) indicated that the two hydroxyl groups and the γ,γ-dimethylallyl group were substituted on the A ring, whereas the methoxyl group and the dimethylchromene ring were on the B ring. Therefore, the A ring had a 5,7-dihydroxy-6-(or 8-)γ,γ-dimethylallyl substitution. The chemical shift of the chelated hydroxyl group of (δ 12.08) suggested the location of the γ,γ-dimethylallyl group to be at C-8. This was confirmed by the following ^{13}C–^{1}H long range correlations in the COLOC spectrum (Fig. 2). The chelated hydroxyl group caused three cross peaks between carbon signals at δ 96.7, 102.0 and 163.9, and the carbon signal at δ 96.7 caused further a cross peak between the aromatic proton (δ 6.08) on the A ring. These findings indicated that no substituent existed at the *ortho*-position of the chelated hydroxyl group at C-5. Consequently the A ring moiety was a 5,7-dihydroxy-8-γ,γ-dimethylallyl substitution. The *ortho*-coupled aromatic proton at δ 6.60 and 7.46 in the ^{1}H NMR spectrum and the methoxyl carbon at δ 62.5 in the ^{13}C NMR spectrum suggested that the methoxyl group was attached at C-2′ and the chromene ring was fused between C-3′ and C-4′. The substitution pattern of the B ring was finally determined by comparison of the chemical shifts of carbons on the B ring of **1** with those of sophoronol (Kim, Ebizuka & Sankawa, 1989; Ohyama, 1995). Thus, the structure of **1** was determined to be 3,5,7-trihydroxy-2′-methoxy-8-γ,γ-dimethylallyl-6‴6‴-dimethylpyrano[2‴3‴:4′,3′]isoflavanone named tetrapterol F.

Compound **2**, obtained as a white powder, mp 168–170°, showed $[M]^+$ at *m/z* 424 in the EIMS which corresponds to the empirical formula, $C_{25}H_{28}O_6$. In the ^{1}H NMR spectrum, three one-proton double doublets at δ 4.43 ($J = 11.0$ and 5.1 Hz), 4.58 ($J = 11.0$ and 9.5 Hz) and 4.18 ($J = 9.5$ and 5.1 Hz) in an ABX system were observed and they were assignable to the protons at C-2 and C-3 in a 2′-oxygenated isoflavanone. The spectrum also showed the presence of two γ,γ–dimethylallyl groups [δ 1.62, 1.65, 1.75 (12H, each *s*, Me×4), 3.19, 3.27 (2H each, *d*, $J = 7.1$ Hz, CH_2×2) 5.25 (2H, *t*, $J = 7.1$ Hz, CH = ×2)] and four hydroxyl groups [δ 8.3, 9.3 (×2) and 12.67 (chelated)]. Fragment ions at *m/z* 221 $[A_1 + H]^+$ (**2a**) and 204 $[B_1]^+$ (**2b**) caused by *retro*-Diels–Alder cleavage in the EIMS (Fig. 3) revealed that each A and B ring had a γ,γ-dimethylallyl group and two hydroxyl groups. Appearance (δ 12.67) of the chelated hydroxyl group at C-5 in a lower field suggested that the position of the γ,γ-dimethylallyl group on the A-ring was at C-6, which was supported by $^{13}C^{1}H$ long range correlations in the COLOC spectrum (Fig. 4). That is, the chelated

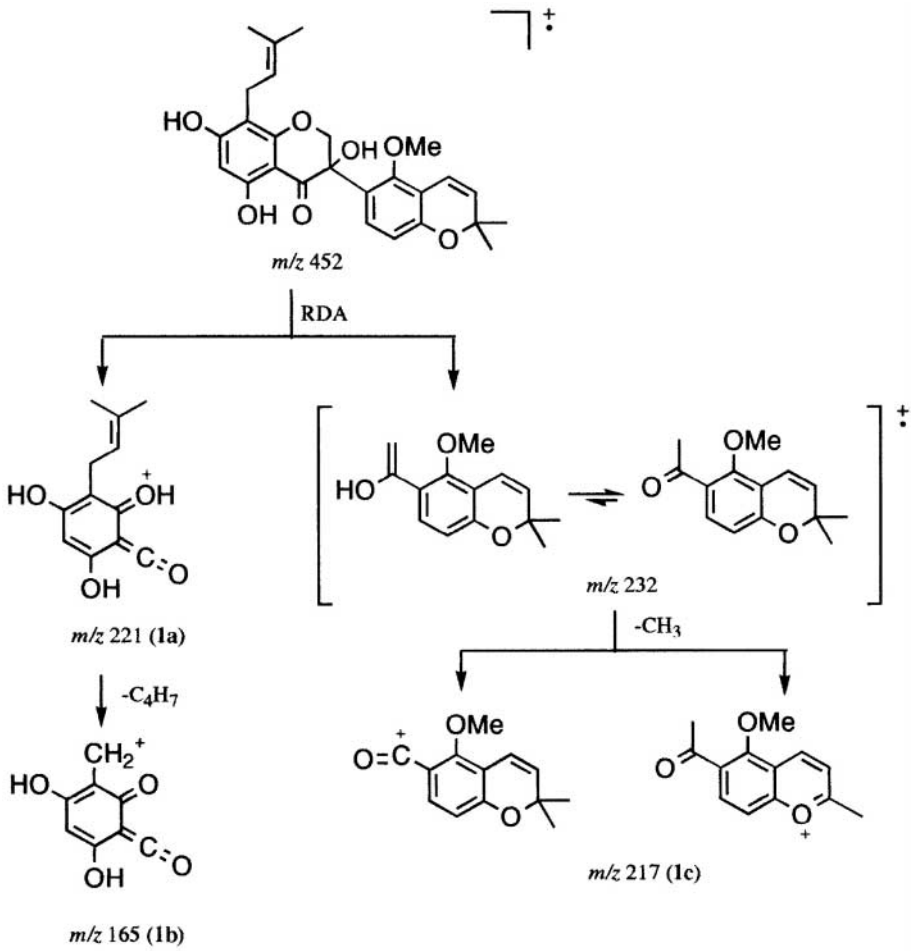


Fig. 1. Mass fragmentation of **1**.

hydroxyl group at C-5 was correlated with three quaternary carbons at δ 103.5, 108.9 and 162.6, and the carbon signal at δ 108.9 was further correlated the methylene proton signal at δ 3.27 assignable to H-1 of the γ,γ-dimethylallyl group. The appearance of two aromatic protons at δ 6.47 and a singlet at 6.82 indicated that the B ring moiety had substituents at the 2′,4′,5′ position. Quaternary carbons bearing hydroxyl groups were resonanced at δ 154.6 and 155.7 in the

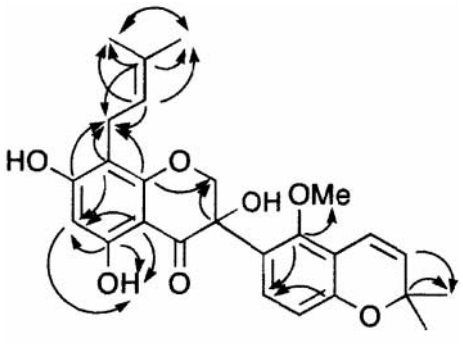


Fig. 2. ^{13}C–^{1}H long range correlations in the COLOC spectrum of **1** (J = 10 Hz).

^{13}C NMR spectrum, indicating that the B ring possessed an oxygenation pattern similar to resorcinol. Hence the B ring moiety has a 2′,4′-dihydroxy-5′-γ,γ-dimethylallyl substitution. The COLOC spectrum showed a cross peak between a carbon at δ 47.3 corresponding to C-3 and the aromatic singlet at δ 6.82, so that the proton was assigned to H-6′. A carbon signal at δ 131.6 was identified to be C-6′ by the correlation with H-6′ in the CH COSY spectrum. The signal at δ 3.19 assignable to the methylene protons of the γ,γ-dimethylallyl group in the COLOC spectrum was correlated with the signals of carbons at δ 131.6, 119.9 and 155.7, which were assigned to C-6′, C-5′ and C-4′, respectively. From these results the γ,γ-dimethylallyl group was located at C-5′. Consequently the structure of **2** was established as 5,7,2′,4′-tetrahydroxy-6,5′-di(γ,γ-dimethylallyl)isoflavanone and named tetrapterol G.

Compound **3** was obtained as a yellow oil, and showed $[M]^+$ at m/z 438 in the EIMS which is equal to the empirical formula $C_{26}H_{30}O_6$. A set of one-proton double doublets at δ 4.22 (J = 5.4 and 9.8 Hz), 4.53 (J = 5.4 and 11.2 Hz) and 4.64 (J = 9.8 and

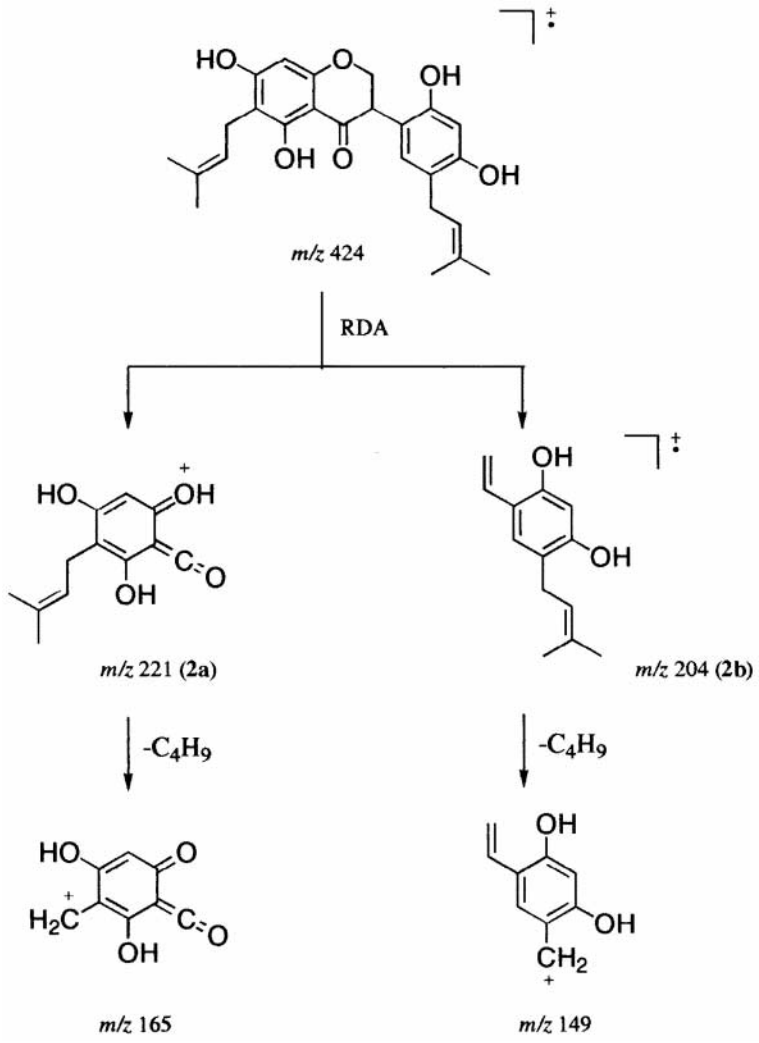


Fig. 3. Mass fragmentation of **2**.

11.2 Hz) assignable to H-3 and H-2 in a 2′-oxygenated isoflavanone skeleton was observed in the ^{1}H NMR spectrum. The spectrum also exhibited the presence of three hydroxyl groups [δ 8.39, 9.52, 12.30 (chelated)], a methoxyl group (δ 3.76) and two γ,γ-dimethylallyl groups [δ 1.62, 1.64 (overlapping), 1.73 (12H, *br s*, Me×4), 3.15 (2H, *br d*, J = 7.3 Hz, CH_2), 3.24 (2H, *br d*, J = 6.8 Hz, CH_2), 5.21 (2H, *t* like *m*, CH = ×2)] in addition to three one-proton singlets at δ 6.03, 6.52 and 6.88. Significant fragments observed at m/z 221 $[A_1 + H]^+$ and 165 $[A_1 - C_4H_7]^+$ in the EIMS showed that the A ring had a 5,7-dihydroxyl substitution with a γ,γ-dimethylallyl group at C-6 or C-8. The chemical shift of a chelated hydroxyl group at C-5 observed at δ 12.30 which was similar to that of kievitone (δ 12.33) (Ohyama, 1995; O'Nell, Adesanya, Roberts & Pantry, 1986) which has a 5,7-dihydroxyl-8-γ,γ-dimethylallyl substitution, whereas the chemical shift of **2** appeared at δ 12.67. These data indicated that the alkyl group was attached at C-8. A fragment ion at m/z 218 $[B_1]^+$ in the EIMS and two aromatic singlets at δ 6.52 and 6.88 suggested that the remaining hydroxyl, methoxyl and γ,γ-dimethylallyl groups were situated in 2′,4′,5′-substitution pattern on the B ring.

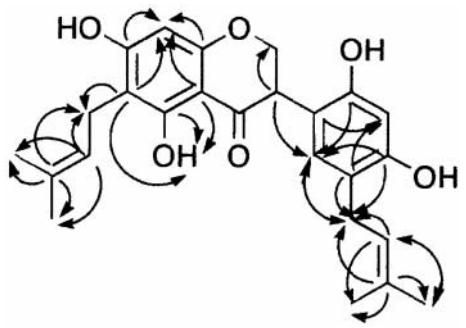


Fig. 4. ^{13}C–^{1}H long range correlations in the COLOC spectrum of **2** (J = 10 Hz).

In the difference NOE spectrum, irradiation of the hydroxyl group at δ 8.39 enhanced both H-3 and the aromatic proton at δ 6.52, indicating that the hydroxyl group was located at C-2′. The methylene protons (δ 3.15) due to the γ,γ-dimethylallyl group and H-3 were enhanced by irradiation of another aromatic proton (δ 6.88) on the B ring, indicating that the alkyl group was located at C-5′. Therefore, the structure of **3** was then characterized as 5,7,2′-trihydroxy-4′-methoxy-8,5′-di(γ,γ-dimethylallyl)isoflavanone and named tetrapterol H.

Compound **4**, obtained as yellow oil, showed $[M]^+$ at m/z 392 in EIMS corresponding to the empirical formula $C_{25}H_{28}O_4$. In the ^{1}H NMR spectrum, a one-proton doublet at δ 3.75 (J = 6.1 Hz) and a two-proton multiplet at δ 4.57 were exhibited in an A_2B-type spin system. The former doublet was assignable to a proton at C-3 of a 2′-deoxygenated isoflavanone skeleton, and the latter multiplet to protons at C-2. The ^{1}H NMR spectrum also exhibited the presence of two hydroxyl groups (δ 8.17 and 9.42) and two γ,γ-dimethylallyl groups [δ 1.66, 1.67, 1.70, 1.72 (3H each, *br s*, Me×4), 3.27 (4H, *br d*, J = 7.3 Hz, CH_2×2), 5.29, 5.32 (1H each, *t* like *m*, CH = ×2)]. Two one-proton singlets at δ 6.43 and 7.60 and fragment ions at m/z 205 $[A_1 + H]^+$ and 149 $[A_1 - C_4H_7]^+$ in the EIMS revealed that **4** had a 7-hydroxy-6-γ,γ-dimethylallyl moiety in the A ring. The cleavage also resulted in fragment ions at m/z 188 $[B_1]^+$ and 133 $[B_1 - C_4H_7]^+$, indicating that the B ring possessed a hydroxyl and a γ,γ-dimethylallyl group. Three aromatic protons at δ 6.76 (1H, *d*, J = 8.3 Hz), 6.93 (1H, dd, J = 2.4 and 8.3 Hz) and 7.02 (1H, *d*, J = 2.4 Hz) in an ABM spin system supported that the B ring had the hydroxyl and the γ,γ-dimethylallyl group at C-4′ and C-3′, respectively. The structure of **4** was consequently determined to be 7,4′-dihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavanone named tetrapterol I.

In addition to **1**–**4**, seven known phenolic constituents were isolated and characterized as lupinifolin (Samlberger, Veleggaar & Welber, 1974), 8-*O*-methylretusin (Jurd, Stevens & Manners, 1972), 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone (Singhal, Sharma, Thyagarajan, Herz & Govindan, 1980), (−)-maackiain (Komatsu, Yokoe & Shirataki, 1978), sophoracarpan A (Kinoshita, Ichinose, Takahashi, Ho, Wu et al., 1990), medicagol (Komatsu et al., 1978) and 2-(2,4-dihydroxyphenyl)-5,6-methylenedioxybenzofuran (Komatsu et al., 1978), respectively, by spectral analysis. As the ^{13}C NMR spectral data of 8-*O*-methylretusin and 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone have not so far been assigned completely, the assignment is shown in Section 3.

3. Experimental

3.1. General

Mps uncorr.; MS: direct inlet, 70 eV, JEOL JMS DX-300; CD: JASCO J-20A; ^{1}H and ^{13}C NMR: JEOL JNM EX-400; 400 and 100 MHz, GX-270; 270 and 67.9 MHz, respectively.

3.2. Plant material

Roots of *Sophora tetraptera* were collected in Auckland, New Zealand in June 1991. The plant was verified by Professor Y. Shirataki and a voucher specimen is deposited at the Herbarium in Josai University has been deposited in the herbarium of that University.

3.3. Extraction and isolation

The air-dried and cut roots of *S. tetraptera* (2.07 kg) were extracted ×3 with MeOH under reflux. The MeOH extract (250 g) after concentration was partitioned with Et_2O and H_2O. The Et_2O layer was concentrated, and the resulting residue (119 g) was chromatographed on silica gel CC with C_6H_6–EtOAc (10:0–1:1) (each fraction was monitored by TLC) to give 8-*O*-methylretusin (430 mg), a mixture of 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone and **2**, a mixture of **1**, **3** and **4**, lupinifolin (4 mg), (−)-maackiain (3.7 g), a mixture of sophoracarpan A and medicagol, 2-(2,4-dihydroxyphenyl)-5,6-methylenedioxybenzofuran (23 mg) in that order. The mixture of 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone and **2** was subjected to low-pressure liquid chromatography (LC) on octadecyl chemically bonded silica gel (ODS) (CPO-HS-221-20, C.I.G. Column system, Kusano Sci. Manufacture Co., Ltd., Japan) eluted with MeOH:H_2O (4:1) to yield 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone (55 mg) and **2** (490 mg). The mixture of **1**, **3** and **4** was further purified by vacuum liquid chromatography ($CHCl_3$:MeOH = 10:1) and prep TLC (hexane:Me_2CO:EtOH = 8:1:1) to give **1** (16 mg), **3** (5 mg) and **4** (7 mg). The mixture of sophoracarpan A and medicagol was rechromatographed on silica gel CC with *n*-hexane:Me_2CO (4:1) to give sophoracarpan A (35 mg) and medicagol (18 mg).

3.4. Compound *1* (tetrapterol F)

Yellow oil; HREIMS m/z 452.1842 for $C_{26}H_{28}O_7$ (calcd 452.1841), EIMS m/z (rel. int.): 452 (M^+, 22), 437 (13), 421 (7), 419 (7), 353 (5), 233 (14), 232 (9), 221 (23), 217 (100), 215 (40), 203 (34), 187 (18), 165 (18); UV λ_{max} (MeOH, nm): 228, 274, 296, 340sh; ^{1}H

Table 1
^{1}H NMR spectral data of tetrapterols F (**1**)–I (**4**) in acetone-d_6.

No.	1	2	3	4
H-2	4.20 (*J* = 12.0 Hz)	4.43 (*dd*, *J* = 11.0, 5.1 Hz)	4.53 (*dd*, *J* = 11.2, 5.4 Hz)	4.57 (2H, m)
H-2	4.71 (*J* = 12.0 Hz)	4.58 (*dd*, *J* = 11.0, 9.5 Hz)	4.64 (*dd*, *J* = 11.2, 9.8 Hz)	
H-3		4.18 (*dd*, *J* = 9.5, 5.1 Hz)	4.22 (*dd*, *J* = 9.8, 5.4 Hz)	3.75 (*d*, *J* = 6.1 Hz)
H-6	6.08 (*s*)		6.03 (*s*)	
H-8		6.02 (*s*)		6.43 (*s*)
H-2′				7.02 (*d*, *J* = 2.4 Hz)
H-3′		6.47 (*s*)	6.52 (*s*)	
H-5′	6.60 (*d*, *J* = 8.5 Hz)			6.76 (*d*, *J* = 8.3 Hz)
H-6′	7.46 (*d*, *J* = 8.5 Hz)	6.82 (*s*)	6.88 (*s*)	6.93 (*dd*, *J* = 8.3, 2.4 Hz)
H-1″	3.23 (2H, *t* like *m*)	3.27 (2H, *br d*, *J* = 7.1 Hz)	3.24 (2H, *br d*, *J* = 6.8 Hz)	3.27 (2H, *br d*, *J* = 7.3 Hz)[d]
H-2″	5.21 (*t* like *m*)	5.25 (*t*, *J* = 7.1 Hz)[a]	5.21 (*t* like *m*)[b]	5.32 (*t* like *m*)
H-4″	1.63 (3H, *s*)	1.65 (3H, *s*)	1.73 (3H, *br s*)	1.72 (3H, *br s*)
H-5″	1.72 (3H, *s*)	1.62 (3H, *s*)	1.64 (3H, *br s*)[c]	1.70 (3H, *br s*)
H-4‴(1‴)	6.53 (*d*, *J* = 10 Hz)	3.19 (2H, *br d*, *J* = 7.1 Hz)	3.15 (2H, *d*, *J* = 7.3 Hz)	3.27 (2H, *br d*, *J* = 7.3 Hz)[d]
H-5‴(2‴)	5.78 (*d*, *J* = 10 Hz)	5.25 (*t*, *J* = 7.1 Hz)[a]	5.21 (*t* like *m*)[b]	5.29 (*t* like *m*)
H-7‴(4‴)	1.39 (3H, *s*)	1.75 (3H, *s*)	1.64 (3H, *br s*)[c]	1.67 (3H, *br s*)
H-8‴(5‴)	1.45 (3H, *s*)	1.65 (3H, *s*)	1.62 (3H, *br s*)	1.66 (3H, *br s*)
OMe	3.63 (3H, *s*)		3.76 (3H, *s*)	
OHs	5.55 (s), 9.58 (*br s*)	8.3, 9.3 (each *br s*)	8.39, 9.52 (each *br s*)	8.17, 9.42 (each *br s*)
C_5-OH	12.08 (*s*)	12.67 (*s*)	12.30 (*s*)	

Values are in ppm (δ_H). Compounds of **1**, **3** and **4** were measured at 400 MHz, and **2** was at 270 MHz.
Figures in parentheses are coupling constants (*J*) in Hz.
[a–d]: overlapping signals.

Table 2
^{13}C NMR spectral data of tetrapterols F (**1**)–I (**4**) in acetone-d_6

No.	1	2	3	4
C-2	75.5	71.0	71.0	72.7
C-3	74.6	47.3	47.1	51.9
C-4	196.7	198.6	198.7	191.1
C-5	163.9	162.6	163.3	128.8
C-6	96.7	108.9	96.4	123.8
C-7	164.9	164.4	164.7	162.7
C-8	108.3	95.0	108.1	102.9
C-9	160.7	162.1	161.2	162.6
C-10	102.0	103.5	103.7	115.0
C-1′	124.7	113.8	114.1	128.4
C-2′	154.6	154.6	155.0	127.6
C-3′	115.1	103.6	100.0	128.7
C-4′	155.5	155.7	158.4	155.0
C-5′	112.3	119.9	121.6	115.7
C-6′	128.7	131.6	132.1	130.6
C-1″	22.0	21.7	22.1	28.2
C-2″	123.7	123.6	123.8	123.2
C-3″	131.2	131.1	131.3	132.9
C-4″	25.8	25.8	25.8	25.9
C-5″	17.8	17.8	17.8	17.8
C-4‴(1‴)	118.4	28.2	28.3	29.0
C-5‴(2‴)	131.0	124.0	123.9	123.5
C-6‴(3‴)	76.2	132.1	131.1	132.4
C-7‴(4‴)	27.0	25.8	25.8	25.8
C-8‴(5‴)	28.3	17.7	17.7	17.8
OMe	62.5		55.6	

Values are in ppm (δ_C).
Compounds of **1**, **3** and **4** were measured at 100 MHz, and **2** was at 67.5 MHz.

and ^{13}C NMR spectral data are shown in Tables 1 and 2.

3.5. Compound **2** (tetrapterol G)

White powder, mp 168–170° (*n*–hexane–Me_2CO); $[\alpha]_D$ 0°, (*c* = 1.0, MeOH); HREIMS *m*/*z* 424.1914 for $C_{25}H_{28}O_6$ (calcd 424.1886); EIMS *m*/*z* (rel. int.): 424 (M^+, 46), 221 (80), 220 (4), 204 (17), 203 (26), 165 (100), 149 (43); IR (KBr, cm^{-1}): 3500–3200 (OH), 2950 (CH), 1640 (C=O), 1600, (arom. C=C); UV λ_{max} (MeOH, nm, log ϵ): 292 (4.26), 336sh (3.53), +$AlCl_3$: 293 (4.23), 342sh (3.51), +NaOAc: 290sh (4.15), 330 (4.46); ^{1}H and ^{13}C NMR spectral data are listed in Tables 1 and 2.

3.6. Compound **3** (tetrapterol H)

Yellow oil; HREIMS *m*/*z* 438.2054 for $C_{26}H_{30}O_6$ (calcd 438.2041), EIMS *m*/*z* (rel. int.): 438 (M^+, 100), 420 (10), 380 (10), 353 (10), 307 (6), 221 (70), 218 (40), 203 (35), 165 (48); UV λ_{max} (MeOH, nm): 225sh, 293, 330sh; ^{1}H and ^{13}C NMR spectral data are shown in Tables 1 and 2.

3.7. Compound **4** (tetrapterol I)

Yellow oil; HREIMS *m*/*z* 392.1988 for $C_{25}H_{28}O_4$ (calcd 392.1984), EIMS *m*/*z* (rel. int.): 392 (M^+, 17), 205 (100), 188 (24), 149 (18), 133 (19); UV λ_{max}

(MeOH, nm): 215, 230sh, 279, 321; ^{1}H and ^{13}C NMR spectral data are shown in Tables 1 and 2.

3.8. 8-O-Methylretusin

Colorless prisms, mp 230–232° (C_6H_6–EtOAc); ^{1}H NMR (DMSO-d_6) δ: 3.80 (3H, *s*, $C_{4'}$–OMe), 3.90 (3H, *s*, C_8–OMe), 7.00 (2H, *d*, J = 8.8 Hz, H-3′,5′), 7.05 (1H, *d*, J = 9.0 Hz, H-6), 7.53 (2H, *d*, J = 8.8 Hz, H-2′,6′), 7.75 (1H, *d*, J = 9.0 Hz, H-5), 8.42 (1H, *s*, H-2), 10.67 (1H, *br s*, C_7–OH); ^{13}C NMR (DMSO-d_6) δ: 55.1 ($C_{4'}$–OMe), 60.7 (C_8–OMe), 113.6 (C-3′,5′), 115.2 (C-6), 117.4 (C-10), 120.7 (C-5), 122.9 (C-3), 124.1 (C-1′), 130.1 (C-2′,6′), 134.7 (C-8), 150.7 (C-9), 153.0 (C-2), 154.7 (C-7), 159.0 (C-4′), 174.7 (C-4).

3.9. 5,7,4′-trihydroxy-6,3′-di(γ,γ-dimethylallyl)isoflavone

Colorless plates, mp 116–117° (MeOH–H_2O); ^{1}H NMR (acetone-d_6) δ: 1.65, 1.71, 1.73, 1.78 (each 3H, each *s*, Me×4), 3.37 (4H, *br d*, J = 7.3 Hz, H-1″, H-1‴), 5.28 (1H, *t*, J = 7.3 Hz, H-2‴), 5.38 (1H, *t*, J = 7.3 Hz, H-2″), 6.48 (1H, *s*, H-8), 6.89 (1H, *d*, J = 8.1 Hz, H-5′), 7.26 (1H, *dd*, J = 8.1, 2.2 Hz, H-6′), 7.34 (1H, *d*, J = 2.2 Hz, H-2′), 8.08 (1H, *s*, H-2), 9.01 (2H, *br s*, OH×2), 13.35 (1H, *s*, C_5–OH); ^{13}C NMR (Me_2CO-d_6) δ: 17.9 (C-5″,5‴), 22.1 (C-1″), 25.9 (C-4″, 4‴), 29.2 (C-1‴), 93.8 (C-8), 106.1 (C-10), 112.4 (C-6), 115.6 (C-5′), 123.2 (C-2″), 123.4 (C-3′), 123.7 (C-2‴), 124.2 (C-3), 128.6 (C-2′), 128.7 (C-1′), 131.3 (C-6′), 131.7 (C-3‴), 132.5 (C-3″), 153.9 (C-2), 155.9 (C-4′), 156.9 (C-9), 160.7 (C-5), 162.6 (C-7), 181.7 (C-4).

Acknowledgements

Y. S. is grateful to Mr. John P. E. McDowell and Miss R. Ishii for providing the samples of *Sophora tetraptera*. The authors thank Mr. S. Yamaguchi for the 270 MHz NMR spectral measurement.

References

Iinuma, M., Ohyama, M., Kawasaka, Y., & Tanaka, T. (1995). *Phytochemistry, 39,* 667.

Jurd, L., Stevens, K., & Manners, G. (1972). *Phytochemistry, 11,* 2535.

Kim, C. K., Ebizuka, Y., & Sankawa, U. (1989). *Chem. Pharm. Bull., 37,* 2879.

Kinoshita, T., Ichinose, K., Takahashi, C., Ho, F.-C., Wu, J.-B., & Sankawa, U. (1990). *Chem. Pharm. Bull., 38,* 2756.

Komatsu, M., Yokoe, I., & Shirataki, Y. (1978). *Chem. Pharm. Bull., 26,* 1274.

Ohyama, M., Ph.D. Thesis, Gifu Pharmaceutical University, Japan, 1995.

O'Nell, M. J., Adesanya, S. A., Roberts, M. F., & Pantry, I. R. (1986). *Phytochemistry, 25,* 1315.

Samlberger, T. M., Veleggaar, R., & Welber, J. C. (1974). *Tetrahedron, 30,* 3927.

Singhal, A. K., Sharma, R. P., Thyagarajan, G., Herz, W., & Govindan, S. V. (1980). *Phytochemistry, 19,* 929.

Tanaka, T., Ohyama, M., Kawasaka, Y., & Iinuma, M. (1994). *Tetrahedron Lett., 35,* 9043.