Chem. Pharm. Bull. 38(6) 1712—1716 (1990) Vol. 38, No. 6

Studies on the Constituents of *Sophora* Species. XXIII.[1] Constituents of the Root of *Sophora chrysophylla* SEEM. (1)[2]

Yoshiaki SHIRATAKI,*,[a] Tomohide TSUZUKU,[a] Ichiro YOKOE,[a] Robert T. HIRANO,[b] and Manki KOMATSU[a]

Faculty of Pharmaceutical Sciences, Josai University,[a] 1-1 Keyakidai, Sakado, Saitama 350-02, Japan and Harold L. Lyon Arboretum, University of Hawaii,[b] 3860 Manoa Rd., Honolulu, Hawaii 96822, U.S.A. *Received December 14, 1989*

Two new isoflavanone, named sophoraisoflavanone C (1), mp 107—109 °C, $C_{30}H_{36}O_5$ and sophoraisoflavanone D (2), mp 118—120 °C, $C_{30}H_{36}O_6$, and a new 6a-hydroxypterocarpan, named (−)-tuberosin (3), mp 203—205 °C, $C_{20}H_{18}O_5$, were isolated from the roots of *Sophora chrysophylla* SEEM. (Leguminosae), together with isoliquiritigenin, 7,4′-dihydroxyflavone, isosophoranone, *l*-maackiain, medicagol and sophoracoumestan A. The structures of 1, 2 and 3 were established to be 5,7,4′-trihydroxy-6-(3,3-dimethylallyl)-3′-geranylisoflavanone, 5,7,2′,4′-tetrahydroxy-6-(3,3-dimethylallyl)-5′-geranylisoflavanone and 6a*S*,11a*S*-3,6a-dihydroxy[2′,2′-dimethylpyrano(5′,6′:8,9)]pterocarpan by means of spectral analysis, respectively.

Keywords *Sophora chrysophylla*; Leguminosae; isoflavanone; 6a-hydroxypterocarpan; sophoraisoflavanone C; sophoraisoflavanone D; (−)-tuberosin; 7,4′-dihydroxyflavone; isosophoranone; sophoracoumestan A

In connection with our previous studies on the phenolics of some plants in the genus *Sophora* (Leguminosae), we have now investigated the constituents of *Sophora chrysophylla* SEEM.[1,2] With regard to the constituents of this plant, alkaloids have been reported from the aerial parts.[3] As described in Experimental, two new isoflavanone, sophoraisoflavanone C (1) and sophoraisoflavanone D (2) and a new 6a-hydroxypterocarpan, (−)-tuberosin (3) were isolated, together with isoliquiritigenin, 7,4′-dihydroxyflavone, isosophoranone, *l*-maackiain, medicagol and sophoracoumestan A, from the methanol extract of the roots of this plant, which was collected in Hawaii Island. This paper deals with the structural elucidation of these compounds.

Sophoraisoflavanone C (1) was obtained as a white powder, mp 107—109 °C, $C_{30}H_{36}O_5$, $[\alpha]_D^{25}$ 0° ($c=1.0$, MeOH), Mg–HCl test (−). It showed hydroxyl (3350 cm^{-1}), carbonyl (1640 cm^{-1}) and aromatic ring (1600 cm^{-1}) absorption bands in the infrared (IR) spectrum. The ultraviolet (UV) spectrum of 1 ($\lambda_{max}^{MeOH}=294$, $340_{(sh)}$ nm) suggested the presence of a flavanone or isoflavanone skeleton. From the negative Mg–HCl test, 1 was considered to be an isoflavanone derivative.

The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of 1 [dimethylsulfoxide-d_6 (DMSO-d_6)] showed the signals of an ABX type grouping due to the C-2 (δ 4.45 and 4.51) and C-3 protons (δ 3.88) in the isoflavanones. It also indicated the presence of one 3,3-dimethylallyl group [δ 1.54, 1.61 (6H, each s, $CH_3 \times 2$, overlapped with a geranyl

TABLE I. NMR Spectral Data for 1 (DMSO-d_6)

Carbon	δ_C	Correlated proton (δ) One-bond	Long-range ($J_{CH}=10$ Hz)
C-1′	125.9 (s)		
C-2′	129.3 (d)	2′-H (6.93, d, $J=2.2$ Hz)	1‴-H_2 (3.19, $J=7.3$ Hz)
C-3′	127.4 (s)		1‴-H_2
C-4′	154.3 (s)		1‴-H_2
C-5′	114.8 (d)	5′-H (6.74, d, $J=8.1$ Hz)	
C-6′	126.6 (d)	6′-H (6.91, dd, $J=2.2$, 8.1 Hz)	
C-1‴	27.7 (t)		2′-H

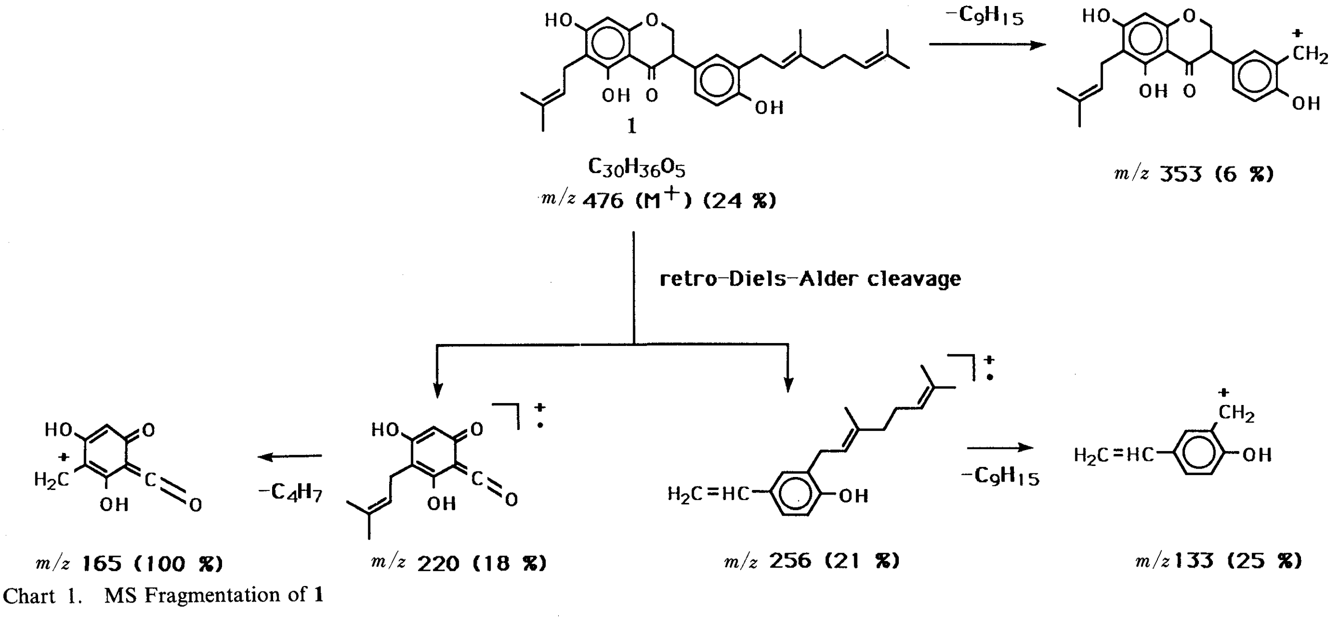


Chart 1. MS Fragmentation of 1

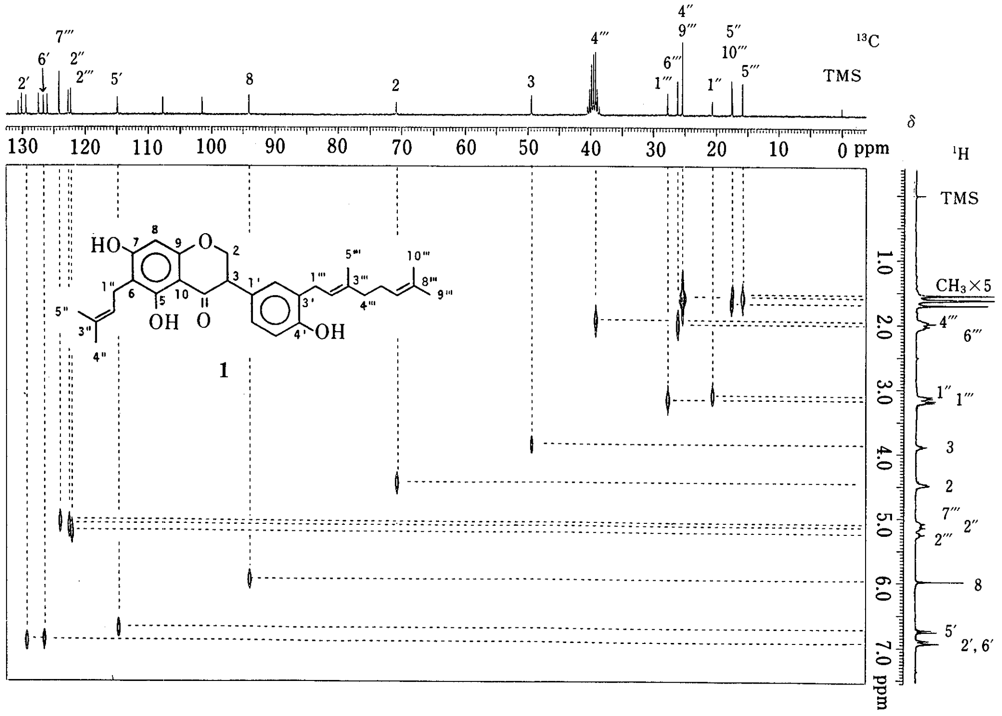


Fig. 1. ^1H–^{13}C Shift Correlated 2-D NMR Sectrum of **1** (DMSO-d_6)

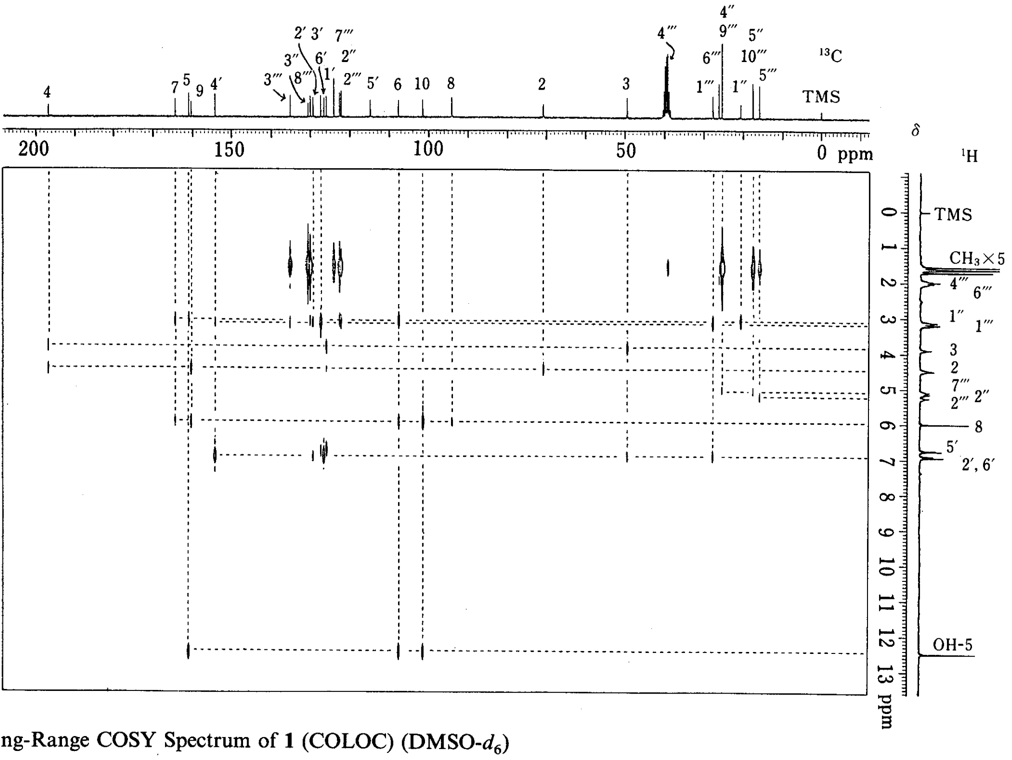
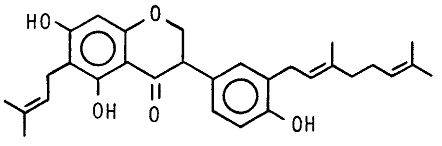
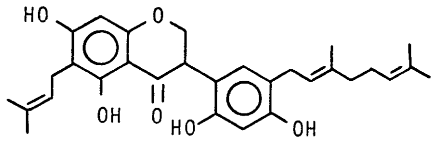


Fig. 2. ^1H–^{13}C Long-Range COSY Spectrum of **1** (COLOC) (DMSO-d_6)

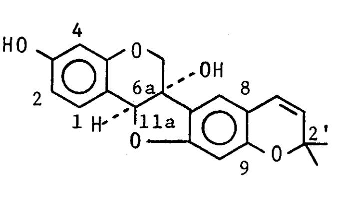
group), 3.12 (2H, d, $J=7.0$ Hz), 5.13 (1H, t $J=7.0$ Hz)], one geranyl (or neryl) group [δ 1.61, 1.69 (9H, each s, $CH_3 \times 3$, overlapped with a 3,3-dimethylallyl group), 1.95 (2H, t, $J=7.0$ Hz), 2.02 (2H, m), 3.19 (2H, d, $J=7.3$ Hz), 5.07 (1H, t, $J=7.0$ Hz), 5.24 (1H, t, $J=7.3$ Hz)] and three hydroxyls [δ 9.34, 10.65 (each 1H) and 12.48 (1H, chelated with C-4 carbonyl); both of which were exchangeable in D_2O]. In the aromatic region of the spectrum, the signals of the remaining four protons appeared as a singlet (δ 5.98, 1H) due to the A-ring proton, and an ABC type grouping [δ 6.74 (1H, d, $J=8.1$ Hz), 6.91 (1H, dd, $J=2.2$, 8.1 Hz) and 6.93 (1H, d, $J=2.2$ Hz)] seemed to be the C-5′, C-6′ and C-2′ protons in the B-ring. The mass spectrum (MS) of **1** showed major ion peaks at m/z 353, 256, 220, 165 and 133. The ion peak at m/z 353 indicated the loss of 123 (C_9H_{15}) mass unit from the molecular ion, suggesting the presence of a geranyl (or neryl) group. The ion peaks at m/z 256 and 220 were derived from a retro-Diels–Alder fragmentation. In view of the ^1H-NMR spectral data, the ion peak at m/z 220 must include the A-ring. This ion loses C_4H_7 to yield the ion



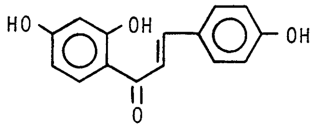
sophoraisoflavanone C (**1**)



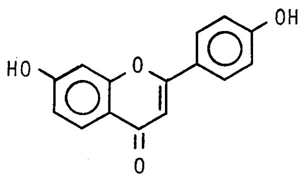
sophoraisoflavanone D (**2**)



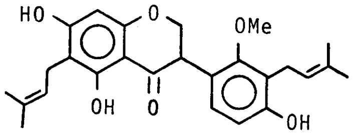
(-)-tuberosin (**3**)



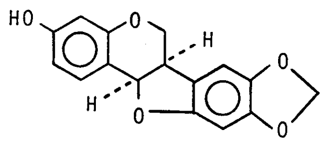
isoliquiritigenin



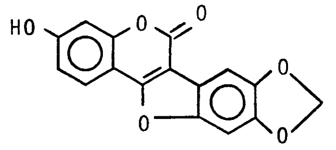
7,4'-dihydroxyflavone



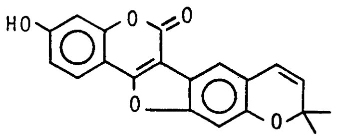
isosophoranone



l-maackiain



medicagol



sophoracoumestan A

peak at m/z 165 and therefore the A-ring contains one 3,3-dimethylallyl group and two hydroxyl groups. On the other hand, the ion peak at m/z 256 arises from the B-ring. It loses C_9H_{15} to yield the peak at m/z 133. Therefore the B-ring contains one geranyl (or neryl) and one hydroxyl group (Chart 1).

Since the ^{13}C-NMR spectrum of **1** (DMSO-d_6) showed δ 70.8 (t) and 49.4 (d), attributed to C-2 and C-3 of isoflavanones, **1** was determined to be an isoflavanone derivative. The position of the 3,3-dimethylallyl group on the A-ring was shown to be at C-6 by the long-range selective proton decoupling (LSPD) method in the ^{13}C-NMR spectrum as follows. In the proton non-decoupled ^{13}C-NMR spectrum with nuclear Overhauser effect (gated decoupling with NOE mode), a signal at δ 94.0 was observed as a doublet (J = 162.0 Hz) which remained unchanged when the chelated hydroxyl proton at the C-5 position (δ 12.48) was selectively irradiated.[4] Therefore, the signal of δ 94.0 could be assigned to the C-8 carbon and the 3,3-dimethylallyl group must be located at C-6. The side chain of B-ring was determined to be at the geranyl group because the ^{13}C-NMR spectrum of **1** showed the signals of C-4''' at δ 40.4 and C-5''' at δ 15.8, respectively.[5] Since three important cross peaks were observed in the ^{1}H–^{13}C shift correlated 2-D NMR (COSY) spectrum of **1**, the carbon signals of δ 129. 3, 114.8 and 126.6 were assigned to the C-2', C-5' and C-6', and the proton signals of δ 6.93, 6.74 and 6.91 were assigned to the 2'-H, 5'-H and 6'-H, respectively. The orientation of the geranyl group was clearly determined by ^{1}H–^{13}C long-range COSY (COLOC) spectral analysis. That is, these 2-D NMR spectra of **1** led to precise assignments of the carbon signals [δ 129.3 (d, C-2'), 127.4 (s, C-3'), 154.3 (s, C-4'), 27.7 (t, C-1''')]. The signal of methylene protons of 1'''-H_2 (δ 3.19) was correlated with the signals of C-2', C-3' and C-4' ($^2J_{C-H}$ and $^3J_{C-H}$) in the COLOC spectrum. The signal of C-1''' was correlated with the proton resonance at δ 6.93 (2'-H, $^3J_{C-H}$) (Figs. 1, 2 and Table I). From these results, it was clear that the geranyl group was located at C-3'.

Consequently the structure of sophoraisoflavanone C (**1**) was established to be 5,7,4'-trihydroxy-6-(3,3-dimethylallyl)-3'-geranylisoflavanone.

Sophoraisoflavanone D (**2**) was obtained as a white powder, mp 118—120 °C, $C_{30}H_{36}O_6$, $[\alpha]_D^{25}$ 0° (c = 1.0, MeOH), Mg–HCl test (−). The UV and IR spectra were very similar to those of **1** and the MS showed the fragment ion at m/z 272 ($C_{18}H_{24}O_2$), which indicated that the B-ring of **2** contains two hydroxyl groups and a geranyl group. The ^{1}H-NMR spectrum of **2** was also similar to that of **1**, except for the signals of δ 6.37 (s) and 6.63 (s) which were assigned to the 3'-H and 6'-H, respectively. Furthermore, a ^{1}H–^{13}C COSY spectral experiment established the above signal assignments. Consequently, the structure of sophoraisoflavanone D (**2**) was concluded to be 5,7,2',4'-tetrahydroxy-6-(3,3-dimethylallyl)-5'-geranylisoflavanone. Although **1** and **2** have an asymmetric carbon, they were isolated as racemates, like many other natural isoflavanones.

(−)-Tuberosin (**3**) was obtained as a white powder, mp 203—205 °C, $C_{20}H_{18}O_5$, $[\alpha]_D^{25}$ −148° (c = 0.5, MeOH). The UV spectrum of **3** showed a characteristic absorption of a 6a-hydroxypterocarpan.[6] Furthermore, the MS of **3** showed remarkable ion peaks at m/z 323 ($M^+ - CH_3$) and m/z 320 ($M^+ - H_2O$). Accordingly, **3** was considered to be a 6a-hydroxypterocarpan derivative having a 2,2-dimethylpyran. The ^{1}H-NMR spectrum of **3** was very similar to that of tuberosin.[6] Furthermore, a ^{1}H–^{13}C COSY and ^{1}H–^{13}C COLOC spectral experiment established the whole signal assignments. After all, **3** was a (−) isomer of tuberosin. About the absolute configurations at C-6a and C-11a, the specific optical rotation of **3** had a (−) sign, **3** most probably has 6a*S* and 11a*S* configurations.[7] From these spectral data, the structure of (−)-tuberosin (**3**) was concluded to be 6a*S*,11a*S*-3,6a-dihydroxy[2′,2′-dimethylpyrano(5′,6′:8,9)] pterocarpan.

Furthermore, isoliquiritigenin,[8] 7,4′-dihydroxyflavone,[9] isosophoranone,[10] *l*-maackiain,[8] medicagol[8] and sophoracoumestant A[11] were also isolated. These are new components of this plant.

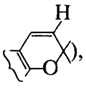
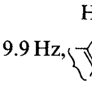
Experimental

All melting points were determined on a Yanagimoto MP-S3 micro melting point apparatus and are uncorrected. IR and UV spectra were taken on Nihon Bunko IR-810 and UVIDEC-430 machines, respectively. ^{1}H- and ^{13}C-NMR spectra were obtained on a JEOL JNM GX-270 FT NMR spectrometer at 270 and 67.9 MHz, respectively, and chemical shifts are given in δ (ppm) with tetramethylsilane (TMS) as an internal standard (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad). The multiplicities (s, d, t, q) of carbon signals were determined by means of gated decoupling with NOE. MS were taken on a JEOL JMS DX-300 mass spectrometer with a direct inlet system. The $[\alpha]_D$ was recorded at 589 nm on a JASCO J-20A spectrometer. Column chromatography was performed on silica gel (Merck, Kieselgel 60 Art. 7734 and Fuji Davison silica gel BW-820 MH). Thin layer chromatography (TLC) was conducted on Wakogel B-5FM and the solvent systems were benzene : ethyl acetate = 1 : 1, *n*-hexane : acetone = 1 : 1, benzene : acetone = 1 : 1. The spots were detected by spraying concentrated H_2SO_4 followed by heating.

Extraction and Separation The dried roots of *Sophora chrysophylla*, which were collected in Hawaii Island in December, 1987 (3.6 kg) were extracted four times with boiling MeOH. The MeOH extract (500 g) was shaken with Et_2O and H_2O. The Et_2O extract was concentrated (186 g) and chromatographed on silica gel using benzene–ethyl acetate (10 : 0—1 : 1) as solvents (each fraction was checked by TLC) to give medicagol (20 mg), sophoracoumestan A (96 mg); isosophoranone (40 mg), sophoraisoflavanone C (80 mg), isoliquilitigenin (40 mg), (−)-tuberosin (60 mg), *l*-maackiain (30 mg), sophoraisoflavanone D (219 mg), 7,4′-dihydroxyflavone (15 mg) in that order.

Sophoraisoflavanone C (1) White powder (*n*-hexane–acetone), mp 107—109 °C, $[\alpha]_D^{25}$ 0° ($c=1.0$, MeOH), Mg–HCl test (−), brown under UV light. MS *m*/*z*: 476.2559 (M^+, Calcd for $C_{30}H_{36}O_5$, 476.2555, 24%), 353 ($C_{21}H_{21}O_5$, 6%), 256 ($C_{18}H_{24}O$, 21%), 220 ($C_{12}H_{12}O_4$, 18%), 165 ($C_8H_5O_4$, 100%), 133 (C_9H_9O, 25%). UV λ_{max}^{MeOH} nm (log ε): 294 (4.17), 340 (sh) (3.64). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 295 (4.23), 340 (sh) (3.54). UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 290 (sh) (3.82), 330 (4.37). IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 1640 (C=O), 1600 (arom. C=C). ^{1}H-NMR (DMSO-d_6), δ: 1.54 (3H), 1.61 (9H), 1.69 (3H) (each s, 4″, 5″, 5‴, 9‴, 10‴-CH_3), 1.95 (2H, t, $J=7.0$ Hz, 4‴-H_2), 2.02 (2H, m, 6‴-H_2), 3.12 (2H, d, $J=7.0$ Hz, 1″-H_2), 3.19 (2H, d, $J=7.3$ Hz, 1‴-H_2), 3.88 (1H, dd, $J=5.5$, 6.6 Hz, 3-H), 4.45 (1H, dd, $J=6.6$, 11.4 Hz, 2-H_{ax}), 4.51 (1H, dd, $J=5.5$, 11.4 Hz, 2-H_{eq}), 5.07 (1H, t, $J=7.0$ Hz, 7‴-H), 5.13 (1H, t, $J=7.0$ Hz, 2″-H), 5.24 (1H, t, $J=7.3$ Hz, 2‴-H), 5.98 (1H, s, 8-H), 6.74 (1H, d, $J=8.1$ Hz, 5′-H), 6.91 (1H, dd, $J=2.2$, 8.1 Hz, 6′-H), 6.93 (1H, d, $J=2.2$ Hz, 2′-H), 9.34, 10.65 (each 1H, each br s, 4′, 7-OH, exchangeable in D_2O), 12.48 (1H, s, 5-OH, exchangeable in D_2O). ^{13}C-NMR (DMSO-d_6), δ: 15.8 (q, C-5‴), 17.4 (q, C-10‴), 17.5 (q, C-5″), 20.6 (t, C-1″), 25.4 (q, C-4″, 9‴), 26.1 (t, C-6‴), 27.7 (t, C-1‴), 40.4 (t, C-4‴), 49.4 (d, C-3), 70.8 (t, C-2), 94.0 (d, C-8), 101.5 (s, C-10), 107.6 (s, C-6), 114.8 (d, C-5′), 122.2 (d, C-2‴), 122.6 (d, C-2″), 124.1 (d, C-7‴), 125.9 (s, C-1′), 126.6 (d, C-6′), 127.4 (s, C-3′), 129.3 (d, C-2′), 130.1 (s, C-3″), 130.6 (s, C-8‴), 135.1 (s, C-3‴), 154.3 (s, C-4′), 160.3 (s, C-9), 160.9 (s, C-5), 164.2 (s, C-7), 196.9 (s, C-4).

Sophoraisoflavanone D (2) White powder (*n*-hexane–acetone), mp 118—120 °C, $[\alpha]_D^{25}$ 0° ($c=1.0$, MeOH), Mg–HCl test (−), brown under UV light. MS *m*/*z*: 492.2516 (M^+, Calcd for $C_{30}H_{36}O_6$, 492.2520, 31%), 369 ($C_{21}H_{21}O_6$, 27%), 272 ($C_{18}H_{24}O_2$, 14%), 220 ($C_{12}H_{12}O_4$, 4%), 165 ($C_8H_5O_4$, 100%), 149 ($C_9H_9O_2$, 31%). UV λ_{max}^{MeOH} nm (log ε): 294 (4.25), 340 (sh) (3.51). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 294 (4.25), 340 (sh) (3.51). UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε):290 (sh) (4.18), 328 (4.48). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1650 (C=O), 1600 (arom. C=C). ^{1}H-NMR (DMSO-d_6), δ: 1.54 (3H), 1.57 (3H), 1.62 (6H), 1.70 (3H) (each s, 4″, 5″, 5‴, 9‴, 10‴-CH_3), 1.93 (2H, t, $J=7.0$ Hz, 4‴-H_2), 1.98 (2H, m, 6‴-H_2), 3.06 (2H, d, $J=7.0$ Hz, 1‴-H_2), 3.12 (2H, d, $J=7.0$ Hz, 1″-H_2), 4.09 (1H, dd, $J=5.5$, 10.3 Hz, 3-H), 4.33 (1H, dd, $J=5.5$, 11.0 Hz, 2-H_{eq}), 4.43 (1H, dd, $J=10.3$, 11.0 Hz, 2-H_{ax}), 5.07 (1H, t, $J=7.0$ Hz, 7‴-H), 5.14 (1H, t, $J=7.0$ Hz, 2″-H), 5.18 (1H, t, $J=7.0$ Hz, 2‴-H), 5.96 (1H, s, 8-H), 6.37 (1H, s, 3′-H), 6.63 (1H, s, 6′-H), 9.18, 9.29, 10.70 (each 1H, each br s, 4′, 2′, 7-OH, exchangeable in D_2O), 12.63 (1H, s, 5-OH, exchangeable in D_2O). ^{13}C-NMR (DMSO-d_6), δ: 15.7 (q, C-5‴), 17.4 (q, C-10‴), 17.5 (q, C-5″), 20.6 (t, C-1″), 25.4 (q, C-4″, 9‴), 26.1 (t, C-6‴), 26.9 (t, C-1‴), 39.1 (t, C-4‴), 46.1 (d, C-3), 69.8 (t, C-2), 94.0 (d, C-8), 102.0 (s, C-10), 102.5 (s, C-3′), 107.5 (s, C-6), 111.9 (s, C-1′), 117.8 (s, C-5′), 122.7 (d, C-2″), 122.9 (d, C-2‴), 124. 1(d, C-7‴), 130.0 (s, C-3″), 130.4 (s, C-6′), 130.5 (s, C-8‴), 134.5 (s, C-3‴), 153.6 (s, C-2′), 154.8 (s, C-4′), 160.6 (s, C-9), 160.9 (s, C-5), 163.8 (s, C-7), 197.6 (s, C-4).

(−)-Tuberosin (3) White powder (*n*-hexane–acetone), mp 203—205 °C, $[\alpha]_D^{25}$ −148° ($c=0.5$, MeOH), brown under UV light. MS *m*/*z*: 338.1155 (M^+, Calcd for $C_{20}H_{18}O_5$, 338.1156, 7%), 323 ($C_{19}H_{15}O_5$, 11%), 320 ($C_{20}H_{16}O_4$, 57%). UV λ_{max}^{MeOH} nm (log ε): 224 (4.74), 280 (4.01), 288 (4.04), 310 (3.99), 324 (sh) (3.97). IR ν_{max}^{KBr} cm^{-1}: 3250 (OH), 1600 (arom. C=C). ^{1}H-NMR (DMSO-d_6), δ: 1.33, 1.35 (each 3H, each s, $CH_3 \times 2$), 3.99 (1H, d, $J=11.4$ Hz, 6-H_{ax}), 4.02 (1H, d, $J=11.4$ Hz, 6-H_{eq}), 5.23 (1H, s, 11a-H), 5.57 (1H, d, $J=9.9$ Hz, ), 6.00 (1H, s, 6a-OH), 6.22 (1H, s, 10-H), 6.24 (1H, d, $J=2.2$ Hz, 4-H), 6.37 (1H, d, $J=9.9$ Hz, ), 6.48 (1H, dd, $J=2.2$, 8.4 Hz, 2-H), 7.09 (1H, s, 7-H), 7.25 (1H, d, $J=8.4$ Hz, 1-H), 9.68 (1H, br s, 3-OH). ^{13}C-NMR (DMSO-d_6), δ: 27.6, 27.7 (each s, $C_{2'}$-$(CH_3)_2$), 69.3 (t, C-6), 75.0 (s, C-6a), 76.2 (s, C-2′), 84.6 (d, C-11a), 98.4 (d, C-10), 102.6 (d, C-4), 109.9 (d, C-2), 111.4 (s, C-1a), 114.4 (s, C-8), 121.6 (d, C-7), 121.7 (d, C-4′), 122.0 (s, C-7a), 127.5 (d, C-3′), 132.2 (d, C-1), 154.7 (s, C-9), 155.6 (s, C-4a), 158.7 (s, C-3), 159.8 (s, C-10a).

Isoliquiritigenin Yellow needles (MeOH–H_2O), mp 203—205 °C. This was identified by direct comparison (mixed melting point, TLC, IR, MS and ^{1}H-NMR) with an authentic sample isolated from *S. tomentosa.*

7,4′-Dihydroxyflavone Pale yellow needles (MeOH–H_2O), mp over 300 °C, blue under UV light. This was identified by direct comparison (mixed melting point, TLC, IR, MS and ^{1}H-NMR) with an authentic sample isolated from *S. subprostrata.*

Isosophoranone White powder (*n*-hexane–acetone), mp 178—181 °C, $[\alpha]_D^{25}$ 0° ($c=1.0$, MeOH). This was identified by direct comparison (mixed melting point, TLC, IR, MS and ^{1}H-NMR) with an authentic sample isolated from *S. tomentosa.*

***l*-Maackiain** White powder (*n*-hexane–acetone), mp 152—154 °C, $[\alpha]_D^{25}$ −189° ($c=0.5$, MeOH). This was identified by direct comparison (mixed melting point, TLC, IR, MS and ^{1}H-NMR) with an authentic sample isolated from *S. moorcroftiana.*

Medicagol Colorless needles (MeOH–$CHCl_3$), mp over 300 °C. This was identified by direct comparison (mixed melting point, TLC, IR, and MS) with an authentic sample isolated from *S. moorcroftiana.*

Sophoracoumestan A Colorless needles (benzene–ethyl acetate), mp over 300 °C. This was identified by direct comparison (mixed melting point, TLC, IR, MS and ^{1}H-NMR) with an authentic sample isolated from *S. franchetiana.*

Acknowledgements We are grateful to Miss S. Matsuoka for her helpful assistance throughout the course of this work. Thanks are also due to Mrs Y. Ishibashi (née Tagaya) and Miss T. Hasegawa for collecting the plant material, and Mr. S. Yamaguchi of Josai University for the NMR spectral measurements. Y. S. is grateful to President T. Matsu-ura, Josai University for a grant to support a part of this work.

References

1) Part XXII: Y. Shirataki, I. Yokoe, M. Noguchi, T. Tomimori, and M. Komatsu, *Chem. Pharm. Bull.*, **36**, 2220 (1988).

2) This work was presented at the 109th Annual Meeting of the Pharmaceutical Society of Japan Nagoya, April 1989, Abstract of Papers, III p. 159.

3) M. M. Kadooka, M. Y. Chang, H. Fukami, P. J. Scheuer, J. Clardy, B. A. Solheim, and J. P. Springer, *Tetrahedron*, **32**, 919 (1976); I. Murakoshi, M. Ito, J. Haginiwa, S. Ohmiya, H. Otomasu, and R. T. Hirano, *Phytochemistry*, **23**, 887 (1984).

4) Y. Shirataki, I. Yokoe, M. Endo, and M. Komatsu, *Chem. Pharm. Bull.*, **33**, 444 (1985).

5) M. Kozawa, N. Morita, K. Baba, and K. Hata, *Yakugaku Zasshi*, **98**, 210 (1978); K. Yakushijin, K. Shibayama, H. Murata, and H. Furukawa, *Heterocycles*, **14**, 397 (1980); T. Nomura, and T. Fukai, *Planta Med.*, **42**, 79 (1981).

6) B. S. Joshi, and V. N. Kamat, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 907.

7) P. M. Dewick, "The Flavonoids, Advances in Research," ed. by J.

B. Harborne and T. J. Mabry, Chapman and Hall, London, 1982, pp. 588.
8) M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.*, **26**, 1274 (1978).
9) Y. Shirataki, I. Yokoe, and M. Komatsu, *J. Nat. Prod.*, **49**, 645 (1986).
10) M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.*, **26**, 3863 (1978).
11) M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.*, **29**, 532 (1981).