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Studies on the Constituents of *Sophora* Species. XIV.[1] Constituents of the Root of *Sophora franchetiana* Dunn (1)[2]

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Three new flavonoid compounds, named sophoraisoflavanone B (I), mp 171—172°, $C_{26}H_{30}O_6$, sophorapterocarpan A (II), mp 149°, $C_{20}H_{20}O_4$, and sophoracoumestan A (III), mp over 300°, $C_{20}H_{14}O_5$, were isolated from the root of *Sophora franchetiana* Dunn (Leguminosae).

Their structures were determined by chemical and spectroscopic studies.

Keywords——*Sophora franchetiana*; Leguminosae; sophoraisoflavanone B; sophorapterocarpan A; sophoracoumestan A; isoflavanone; pterocarpan; coumestan; prenylflavonoid

In the previous papers,[1] we reported the isolation and structural elucidation of a number of flavonoids from *Sophora subprostrata*, *S. flavescens* (*S. angustifolia*), *S. japonica* and *S. tomentosa*.

In our further studies on these series ,three new compounds, named sophoraisoflavanone B (I), sophorapterocarpan A (II) and sophoracoumestan A (III) have been isolated from the root of *Sophora franchetiana* Dunn (Japanese name, Tsukushimuresuzume). This paper deals with the structural elucidation of these compounds.

Sophoraisoflavanone B (I) was obtained as colorless needles, mp 171—172°, $[\alpha]_D^{22}$ 0° (EtOH), $M^+=438.2056$ (Calcd for $C_{26}H_{30}O_6$: 438.2043), $C_{26}H_{30}O_6$, exhibiting negative Mg–HCl test, positive ferric chloride reaction and positive Gibbs reaction. The infrared (IR) spectrum of I suggested the presence of hydroxyl (3400 cm^{-1}), carbonyl (1640 cm^{-1}) groups and aromatic ring (1610 cm^{-1}) and the ultraviolet (UV) spectrum ($\lambda_{max}^{EtOH}=295$, $340_{(sh)}$nm) suggested the presence of a flavanone or isoflavanone skeleton in I.[3a)] From the negative Mg–HCl test, I was considered to be an isoflavanone derivative.

The proton magnetic resonance (PMR) spectrum of I [$CDCl_3$] showed δ 4.6—4.8 (2H, m) and δ 3.96 (1H, t, $J=5.2$ Hz) attributed to the C-ring protons (C_2–H_2, C_3–H) of the isoflavanone. It also indicated the presence of two γ,γ-dimethylallyl groups [δ 1.67, 1.70, 1.77 (12H, each s, $(C\underline{H}_3)_2\times2$), δ 3.1—3.3 (4H, m, Ar–$C\underline{H}_2$–CH=$\times2$), δ 5.1—5.3 (2H, m, Ar–CH_2–$C\underline{H}$=$\times2$)], one methoxyl group [δ 3.76 (3H, s)], three hydroxyl groups [δ 7.7—7.9 (2H), 12.1 (1H, s, chelated with 4-carbonyl); both disappeared on the addition of D_2O] and three aromatic protons [δ 6.00 (1H, s, C_6 or C_8–H), δ 6.48 (1H, s, $C_{3'}$–H), δ 7.11 (1H, s, $C_{6'}$–H)].

The mass spectrum (MS) of I (Chart 1) showed major ions at *m/e* 382 (20%), 220 (10%) and 218 (43%). The ions at *m/e* 220 and 218 were derived from a retro-Diels–Alder fragmentation. In view of the PMR spectral data, the ion at *m/e* 220 must include the A-ring. This ion loses C_4H_7 to yield *m/e* 165 (100%) and therefore contains one γ,γ-dimethylallyl group. On the other hand, the ion at *m/e* 218 arises from the B-ring. It loses CH_3 and C_4H_7 to yield *m/e* 203 (68%) and 163 (19%), respectively. Therefore the B-ring contains one methoxyl and one γ,γ-dimethylallyl groups.

From these data, it is clear that there are two γ,γ-dimethylallyl groups in I, one being attached to the A-ring and the other to the B-ring.

Since the ^{13}C-nuclear magnetic resonance (CMR) spectrum of I showed δ 69.7 (t) and 46.3 (d), attributed to C-2 and C-3 of isoflavanones, I was determined to be an isoflavanone

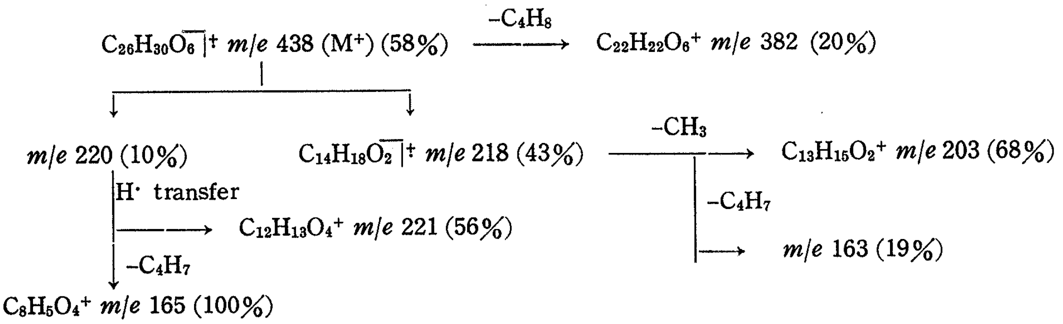
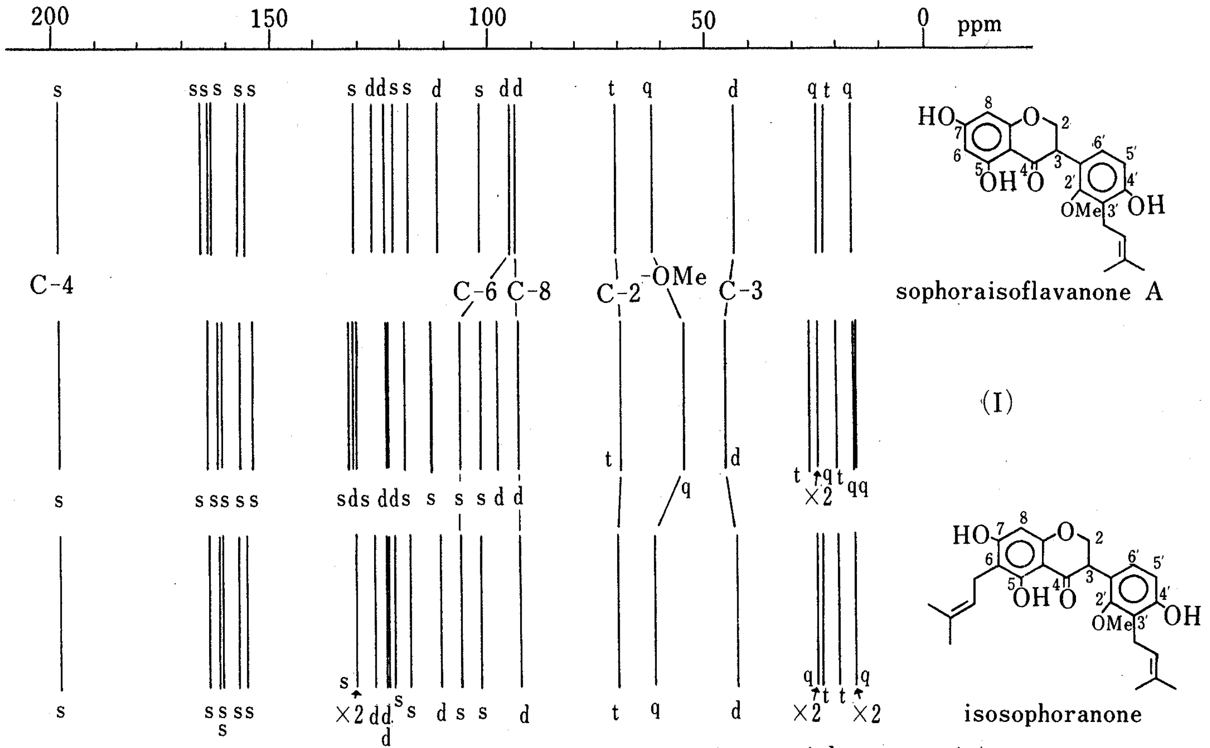


Chart 1. MS Fragmentation of I



off-resonance decoupling (SFORD). s,singlet; d,doublet; t,triplet; q,quartet

Fig. 1. CMR Spectrum of I (in DMSO-d_6)

derivative. The signals of δ 107.9 (C-6) and 94.3 (C-8) are the same as those of isosophoranone, and the γ,γ-dimethylallyl group (A-ring) was shown to be located at C-6 (Fig. 1).

Accordingly, the above results provide the following partial formula for I (Fig. 2).

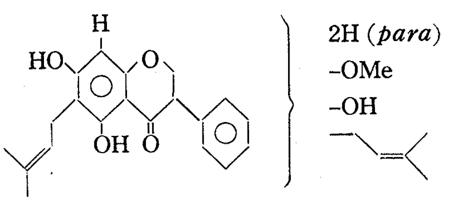


Fig. 2

That is to say, there are six possibilities for the substitution patterns of I in the B-ring (Fig. 3).

Dewick *et al.*[4] have reported that the "biosynthesis of pterocarpan and coumestan" proceeds *via* isoflavone, followed by 2′-hydroxylation and reduction to isoflavanone. This isoflavanone is reduced to isoflavan-4-ol which can then cyclize to pterocarpan and coumestan.

The biosynthetic analogy to the other prenylflavonoids isolated from *Sophora* species suggested that the B-ring has a 2′,4′-dioxygenated pattern. Therefore, the partial formulae (c) to (f) of the B-ring in I were excluded.

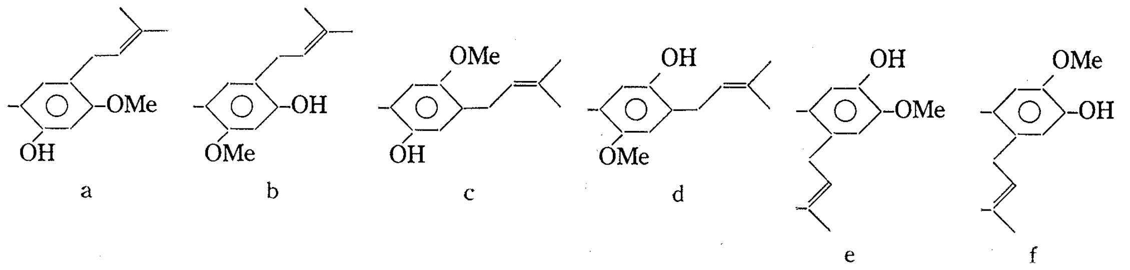


Fig. 3. Possible Partial Formulae of the B-ring in I

Consequently, the partial formula of B-ring in I was determined to be either (a) or (b). On refluxing a solution of I in methanolic hydrochloric acid, the γ,γ-dimethylallyl side chain cyclized with the neighboring hydroxyl group to afford three products (Ia, Ib and Ic). Their structures were formulated from their spectral characteristics in the following way.

The first product (Ia), exhibiting a positive Gibbs reaction, showed M^+ at *m/e* 438 in the MS, and the PMR spectrum revealed the presence of one 2,2-dimethylchroman [δ 1.33 (6H, s, $_{-\mathrm{O}}^{\;\mathrm{C}}\!\!>\!\mathrm{C(C\underline{H}_3)_2}$), δ 1.6—1.8 (8H, m, Ar–$\mathrm{CH_2}$–$\mathrm{C\underline{H}_2}$– overlapped $\mathrm{C{=}C(C\underline{H}_3)_2}$), δ 2.57 (2H, t, $J=$ 6 Hz, Ar–$\mathrm{C\underline{H}_2}$–$\mathrm{CH_2}$)] and one γ,γ-dimethylallyl group [δ 1.6—1.8 (8H, m, $\mathrm{C{=}C(C\underline{H}_3)_2}$ overlapped Ar–$\mathrm{CH_2}$–$\mathrm{C\underline{H}_2}$–), δ 3.20 (2H, br. d, $J=7$ Hz, Ar–$\mathrm{C\underline{H}_2}$–CH=C), δ 5.1 (1H, br. t, $J=7$ Hz, –$\mathrm{CH_2}$–$\mathrm{C\underline{H}{=}C\langle}$)].

The presence of 2,2-dimethylchroman in the A-ring and a $\gamma,\gamma,$-dimethylallyl group in the B-ring was determined as follows.

The PMR spectra of Ia were compared with those of dicycloisosophoranone A[5] and the cyclized product of sophoraisoflavanone A (cyclosophoraisoflavanone A,[1] which was produced by acid treatment of sophoraisoflavanone A).

Dicycloisosophoranone A showed the signal of benzylic methylene protons of 2,2-dimethylchroman in the A-ring at δ 2.58 and that of the B-ring at δ 2.84.[6] Cyclosphoraisoflavanone A exhibited that of the B-ring at δ 2.84, and Ia showed a signal at δ 2.57.

From these data, it is clear that the signal of benzylic methylene protons of 2,2-dimethylchroman in the A-ring appeared at around δ 2.57 and in the B-ring at δ 2.84 (in $CDCl_3$) in these isoflavanones.

Accordingly, the cyclized product could be formulated as Ia.

The second product (Ib) and the third product (Ic) also exhibited positive Gibbs reaction and showed M^+ at *m/e* 470 ($C_{26}H_{30}O_6+CH_3OH$) and 456 ($C_{26}H_{30}O_6+H_2O$) in the MS, respectively.

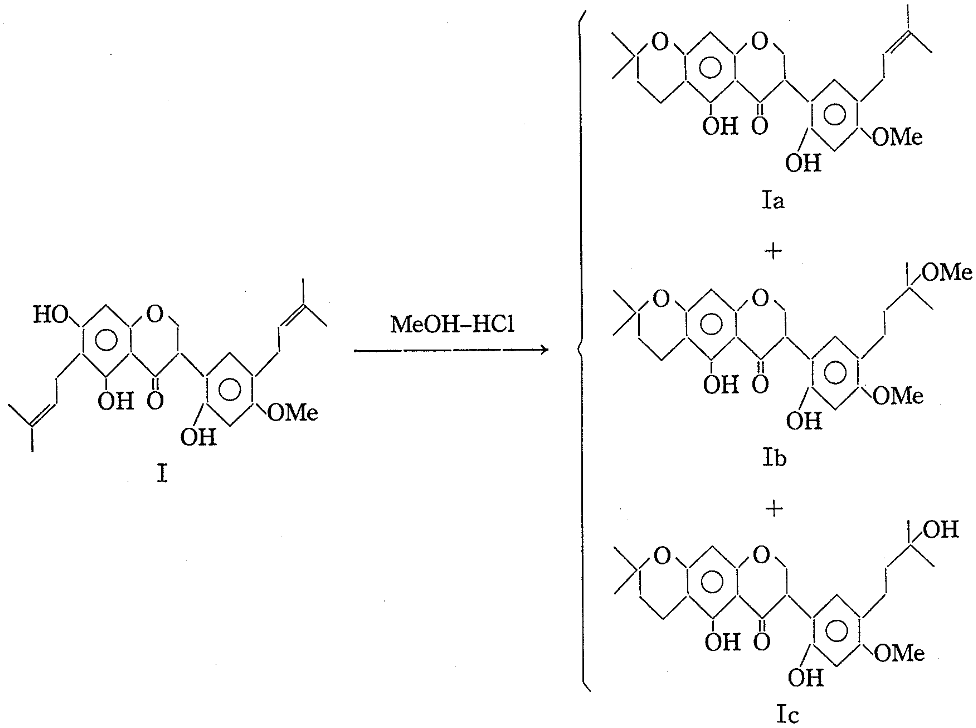
The PMR spectra of Ib and Ic showed the signals of benzylic methylene protons of 2,2-dimethylchroman at δ 2.4—2,7, not at around δ 2.84 (see "Experimental").

From these spectral data, a γ,γ-dimethylallyl side chain cyclized in the A-ring ,and methanol and water were added to the γ,γ-dimethylallyl group in the B-ring (Ib and Ic), suggesting that the γ,γ-dimethylallyl group in the B-ring is not located adjacent to a hydroxyl group[7] (Fig. 4).

This ruled out the formula (b) which could give two 2,2-dimethylchroman in the A-ring and B-ring. This indicated the structure of the B-ring to be (a).

Consequently, sophoraisoflavanone B is represented by the structure I. Although sophoraisoflavanone B has an asymmetric carbon, it was isolated as a racemate, like other natural isoflavanones.[8]

Sophorapterocarpan A (II) was obtained as colorless needles, mp 149°, $[\alpha]_D^{22}$ $-187°$ (EtOH), $M^+=324.1342$ (Calcd for $C_{20}H_{20}O_4$: 324.1359), $C_{20}H_{20}O_4$. It gave hydroxyl and aromatic ring absorption bands in the IR spectrum. The UV spectrum indicated a pterocarpan structure, with an absorption maximum at 290 nm.


I

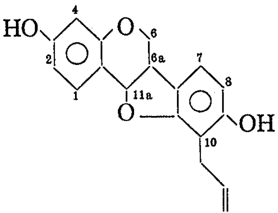
Ia

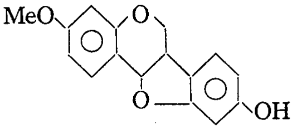
Ib

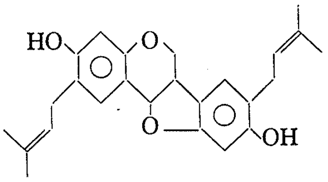
Ic

Fig. 4. Acid Treatment of I

Table I. PMR Spectral Data for Pterocarpans (δ) ppm (in $CDCl_3$)


phaseollidin


9-hydroxy-3-methoxy-pterocarpan


ficifolinol

	1-H	2-H	4-H	6-H	6a-H	7-H	8-H	10-H	11a-H
II	7.38	6.54	6.41	3.5—3.8 4.2—4.3		6.95 (s)		6.36 (s)	5.3—5.5
Phaseollidin	7.37	6.53	6.40	3.63 4.21	3.54	6.93 (d)	6.36 (d)		5.44
9-Hydroxy-3-methoxypterocarpan	7.45	6.66	6.4	4.24		7.1	6.4	6.4	5.52
Ficifolinol	7.16		6.32	3.62 4.12	3.36	6.86		6.28	5.34

The MS of II exhibited ions at *m/e* 324 (M^+, 97%) and *m/e* 269 ($M^+ - C_4H_7$, 100%) suggesting one γ,γ-dimethylallyl group.

The PMR spectrum of II showed a complex pattern characteristic of heterocyclic ring protons in pterocarpans at δ 3.5—3.8, δ 4.2—4.3, δ 5.3—5.5[9] and the presence of one γ,γ-dimethylallyl group [δ 1.78 (6H, s), 3.29 (2H, br. d, $J=7.4$ Hz), 5.3—5.5 (2H, m, $-CH_2-C\underline{H}=$, $C_{11a}-H$, overlapped)], and two hydroxyls [δ 5.05 (1H, s), δ 5.18 (1H, s); disappeared on the addition of D_2O].

The substitution pattern of these functional groups was determined by comparing the PMR spectra of pterocarpan derivatives, phaseollidin,[10] 9-hydroxy-3-methoxypterocarpan[11] and ficifolinol[12] (Table I).

It is clear that two hydroxyls were located at positions 3 and 9, as expected on biogenetic grounds.[4]

Consequently, the γ,γ-dimethylallyl group of II must be located at position 2 or 8. If it is assumed that the γ,γ-dimethylallyl group is located at position 2, the proton signals of 1-H and 4-H would be observed at δ 7.16 and δ 6.32, as in ficifolinol, and the proton signals of 7-H, 8-H and 10-H would be observed at δ 7.1 and δ 6.4, as in 9-hydroxy-3-methoxypterocarpan. However, such signals of II were not observed. In addition, II was compared with phaseollidin, and the PMR data were in good agreement, except for 7-H, 8-H of phaseollidin which appear as doublets (J=9 Hz) and 7-H, 10-H of II, which appear as singlets.

Therefore the γ,γ-dimethylallyl group is located at position 8.

Since the specific optical rotation of II was −187° (EtOH), the absolute configuration of II was determined as 6a*R*, 11a*R*, like those of other major pterocarpans.[3b] In conclusion, the structure of sophorapterocarpan A has been established as II.

Sophoracoumestan A (III) was obtained as colorless needles, mp over 300°, M^+=334.0819 (Calcd for $C_{20}H_{14}O_5$: 334.0839) $C_{20}H_{14}O_5$.

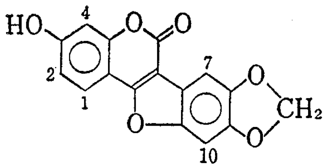
It gave the absorption bands of hydroxyl (3400 cm^{-1}) and α-pyrone (1710 cm^{-1}) moieties in the IR spectrum. The UV spectrum indicated a coumestan structure, with absorption maxima at 255, 308 and 373 nm.

The PMR spectrum of III showed one 2,2-dimehtylchromene ring [δ 1.43 (6H, s, $CH_3 \times 2$), δ 5.85 (1H, d, J=10 Hz), δ 6.63 (1H, d, J=10 Hz)] and one hydroxyl group [δ 10.7 (1H, s); disappeared on the addition of D_2O].

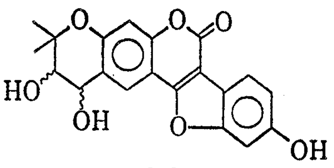
The substitution pattern of these functional groups was determined by comparison of the PMR spectra of coumestan derivatives, medicagol and corylidin[13] (Table II).

It is clear that the substitution pattern involves a 3,9-di-O-function, as expected on biogenetic grounds from the biosynthetic route of coumestan, as reported by Dewick.[4]

TABLE II. PMR Spectral Data for Coumestans (δ) ppm (in DMSO-d_6)

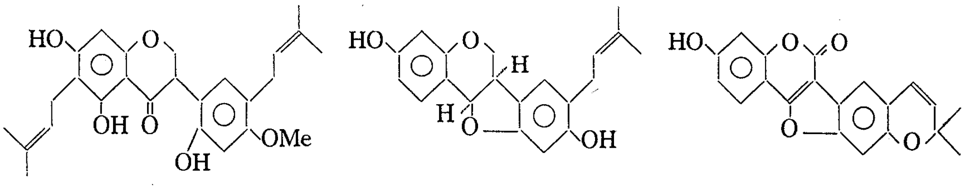


medicagol



corylidin

	1-H	2-H	4-H	7-H	8-H	10-H
III	7.85	6.9—7.0		7.61 (s)		7.24 (s)
Medicagol	7.82	6.9—7.0		7.48 (s)		7.30 (s)
Corylidin	7.86 (s)		6.99 (s)	7.65	6.89	7.12



sophoraisoflavanone B
I

sophorapterocarpan A
II

sophoracoumestan A
III

Fig. 5

Consequently, the 2,2-dimethylchromene ring of III must be located at position 2 or 8. If the 2,2-dimethylchromene ring is located at position 2, the proton signals of 7-H, 8-H and 10-H would be observed at δ 7.65, δ 6.89 and δ 7.12, as in corylidin. However, such signals of III were not observed. Therefore, 2,2-dimethylchromene was located at position 8. This is consistent with the biosynthesis of pterocarpan and coumestan *via* isoflavanone in *Sophora* species.

From these spectral data and biogenetic considerations, the structure of sophoracoumestan A was concluded to be III.

Experimental

All melting points were determined with a Yanagimoto MP-S3 micro melting point apparatus, and are uncorrected. IR and UV spectra were recorded on a Nihon Bunko model IRA-1 spectrometer and a UVIDEC-1 spectrometer, respectively. PMR and CMR spectra were measured at 100 MHz with a JNM-PS-100 spectrometer and at 25 MHz with a JNM-PFT-100 NMR spectrometer, respectively; chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad). MS were taken on a Hitachi RMU-7M mass spectrometer with a direct inlet system.

Column chromatography was carried out with Wakogel C-200 (Wako Pure Chemical Ind. Ltd.). Thin-layer chromatography (TLC) was conducted on Kieselgel G nach Stahl (Merck) and the spots were detected by spraying Gibbs reagent or conc. H_2SO_4, followed by heating.

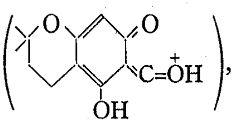
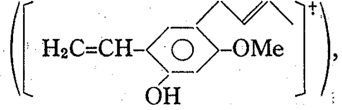
The ratios of solvents and reagents in the mixtures are given in v/v.

Extraction and Separation——The dried roots of *Sophora franchetiana* Dunn, which had been collected in Miyazaki prefecture (112 g) in Oct., 1978, were extracted five times with boiling MeOH. The ether-soluble part (10 g) of the MeOH extract was chromatographed on silica gel with benzene and benzene–AcOEt as solvents to give I (123 mg), *l*-maackiain (40 mg), II (214 mg) and III (4 mg).

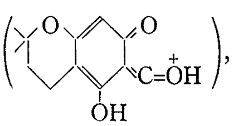
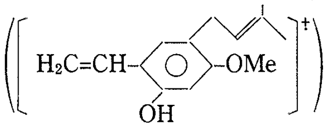
Sophoraisoflavanone B (I)——I was recrystallized from benzene as colorless needles, mp 171—172°, $[\alpha]_D^{22}$ 0° (c=0.3, EtOH), brown under UV light, greenish-brown with $FeCl_3$, blue in the Gibbs reaction. Mg-HCl (−). TLC *Rf*: 0.72 (benzene–AcOEt=1: 1) (solv. 1). MS *m/e*: 438.2056 (M^+, Calcd for $C_{26}H_{30}O_6$: 438.2043) base peak, 382.1429 ($C_{22}H_{22}O_6$: 382.1417), 221.0813 ($C_{12}H_{13}O_4$: 221.0813), 218.1294 ($C_{14}H_{18}O_2$: 218.1306), 203.1084 ($C_{13}H_{15}O_2$: 203.1073), 165.0188 ($C_8H_5O_4$: 165.0188). UV λ_{max}^{EtOH} nm (log ε): 295 (4.31), $340_{(sh)}$ (3.62). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1640 (C=O), 1610 (arom. C=C), 1380 (CH_3). PMR ($CDCl_3$): 1.67, 1.70, 1.77 (12H, each s, $(C\underline{H}_3)_2\times 2$), 3.1—3.3 (4H, m, $Ar–C\underline{H}_2–CH=\times 2$), 3.76 (3H, s, $–OC\underline{H}_3$), 3.96 (1H, t, J=5.2 Hz, C_3–H), 4.6—4.8 (2H, m, $C_2–H_2$), 5.1—5.3 (2H, m, $Ar–CH_2–C\underline{H}=\times 2$), 6.00 (1H, s, C_8–H), 6.48 (1H, s, $C_{3'}$–H), 7.11 (1H, s, $C_{6'}$–H), 7.7—7.9 (2H, br, OH×2; disappeared on the addition of D_2O), 12.1 (1H, s, C_5–OH; disappeared on the addition of D_2O). CMR (DMSO-d_6): 17.4 (q, $\underline{C}H_3$), 17.6 (q, $\underline{C}H_3$), 20.7 (t, $–\underline{C}H_2–CH=C\langle$), 25.4 (q, $\underline{C}H_3\times 2$), 27.2 (t, $–\underline{C}H_2–CH=C\langle$), 46.3 (d, C-3), 55.2 (q, $O\underline{C}H_3$), 69.7 (t, C-2), 94.3 (d, C-8), 99.2 (d, C-3′), 102.2 (s, C-4a), 107.9 (s, C-6), 113.2 (s, C-5′), 119.6 (s, C-1′), 123.0 (d, $–\underline{C}H=C\langle$), 123.2 (d, $–\underline{C}H=C\langle$), 130.5 (s, $–CH=\underline{C}\langle$), 130.8 (d, C-6′), 131.4 (s, $–CH=\underline{C}\langle$), 154.5 (s, C-2′), 157.2 (s, C-4′), 161.0 (s, C-8a), 161.3 (s, C-5), 164.4 (s, C-7), 198.0 (s, CO).

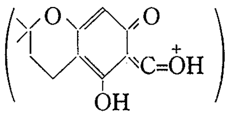
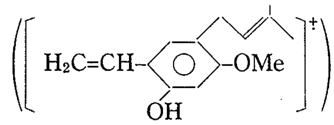
Acid Treatment of I (Formation of Ia, Ib and Ic)——After the addition of conc. HCl (2 ml) to a solution of I (34 mg) in MeOH (10 ml), the mixture was refluxed for 4 hr on a water-bath. The reaction mixture was diluted with water and extracted with ether. The ether layer was washed with water, dried over anhyd. Na_2SO_4 and concentrated to dryness.

The crude products were then chromatographed on a silica gel column with benzene as an eluting solvent, to give Ia (2 mg), Ib (18 mg) and Ic (4 mg).

Compound Ia was obtained as an amorphous powder. Gibbs reaction (+). PMR ($CDCl_3$): 1.33 (6H, s, ${}^{C}_{-O}{>}C(C\underline{H}_3)_2$), 1.6—1.8 (8H, m, $C=C(C\underline{H}_3)_2$, $Ar–CH_2–C\underline{H}_2–$), 2.57 (2H, t, J=6 Hz, $Ar–C\underline{H}_2–CH_2–$), 3.20 (2H, br.d, J=7 Hz, $Ar–C\underline{H}_2–CH=\langle$), 3.78 (3H, s, $–OCH_3$), 3.90 (1H, t, J=4 Hz, C_3–H), 4.6—4.8 (2H, m, $C_2–H_2$), 5.1 (1H, br.t, J=7 Hz, $–CH_2–C\underline{H}=C\langle$), 5.92 (1H, s, C_8–H), 6.50 (1H, s, $C_{3'}$–H), 7.23 (1H, s, $C_{6'}$–H), 7.8 (1H, br, –OH; disappeared on the addition of D_2O), 12.0 (1H, s, C_5–OH; disappeared on the addition of D_2O). MS *m/e*: 438 (M^+), 383 ($M^+-C_4H_7$), 221 , 218 , 203 ($218-CH_3$), 165 ($221-C_4H_7$).

Compound Ib was obtained as an amorphous powder. Gibbs reaction (+). PMR ($CDCl_3$): 1.20 (6H, s, ${}^{C}_{MeO}{>}C(C\underline{H}_3)_2$), 1.34 (6H, s, ${}^{C}_{-O}{>}C(C\underline{H}_3)_2$), 1.6—1.8 (4H, m, $Ar–CH_2–C\underline{H}_2–\times 2$), 2.4—2.7 (4H, m, $Ar–C\underline{H}_2–$

CH_2−×2), 3.22 (3H, s, $(CH_3)_2C\langle^{C}_{OC\underline{H}_3}$), 3.77 (3H, s, $-OCH_3$), 3.91 (1H, t, $J=4$ Hz, C_3–H), 4.6—4.9 (2H, m, C_2–H_2), 5.93 (1H, s, C_8–H), 6.50 (1H, s, $C_{3'}$–H), 7.22 (1H, s, $C_{6'}$–H), 7.90 (1H, br, –OH; disappeared on the addition of D_2O), 12.0 (1H, s, C_5–OH; disappeared on the addition of D_2O). MS *m/e*: 470 (M^+), 438 (M^+-CH_3OH), 383 ($M^+-C_4H_7$), 221  , 218  , 203 ($218-CH_3$), 165 ($221-C_4H_7$).

Compound Ic was obtained as an amorphous powder. Gibbs reaction (+). PMR ($CDCl_3$): 1.27 (6H, s, $^{C}_{HO}\rangle C(C\underline{H}_3)_2$), 1.34 (6H, s, $^{C}_{-O}\rangle C(C\underline{H}_3)_2$), 1.6—1.8 (4H, m, Ar–$CH_2$–$C\underline{H}_2$–×2), 2.5—2.7 (4H, m, Ar–$C\underline{H}_2$–CH_2–×2), 3.78 (3H, s, $-OCH_3$), 3.91 (1H, t, $J=4$ Hz, C_3–H), 4.7—4.9 (2H, m, C_2–H_2), 5.94 (1H, s, C_8–H), 6.51 (1H, s, $C_{3'}$–H), 7.24 (1H, s, $C_{6'}$–H), 8.0 (1H, br, –OH; disappeared on the addition of D_2O), 12.0 (1H, s, C_5–OH; disappeared on the addition of D_2O). MS *m/e*: 456 (M^+), 438 (M^+-H_2O), 383 ($M^+-C_4H_7$), 221  , 218  , 203 ($218-CH_3$), 165 ($221-C_4H_7$).

Sophorapterocarpan A (II)——II was recrystallized from benzene as colorless needles, mp 149°, $[\alpha]^{22}_{D}$ −187° ($c=0.3$, EtOH). TLC *Rf*: 0.69 (solv. 1). MS *m/e*: 324.1342 (M^+, Calcd for $C_{20}H_{20}O_4$: 324.1359) base peak, 269.0808 ($C_{16}H_{13}O_4$: 269.0811), 147.0465 ($C_9H_7O_2$: 147.0445), 123.0441 ($C_7H_7O_2$: 123.0444). UV λ^{EtOH}_{max} nm (log ε): 290 (3.96). IR ν^{KBr}_{max} cm^{-1}: 3400 (OH), 1620, 1600, 1520 (arom. C=C), 1390 (CH_3). PMR (Table I).

Acetylation of II (IIa)——A solution of II (50 mg) in dry pyridine (3 ml) and acetic anhydride (2 ml) was allowed to stand overnight at room temperature, then the reaction mixture was worked up in the usual manner. IIa (30 mg) was obtained as an oily product, giving no color with $FeCl_3$. IR $\nu^{CHCl_3}_{max}$ cm^{-1}: 1760, 1210, 1150 (ester), 1620, 1600, 1510, 1490 (arom. C=C), 1380 (CH_3). PMR ($CDCl_3$): 1.70, 1.75 (each 3H, each s, CH_3×2), 2.28 (6H, s, –OAc×2), 3.15 (2H, br.d, $J=7.4$ Hz, Ar–$C\underline{H}_2$–CH=), 3.5—3.6 (1H, m, C_{6a}–H), 3.73 (1H, d, $J=10$ Hz, C_{6ax}–H), 4.31 (1H, dd, $J=10$ Hz, 3.3 Hz, C_{6eq}–H), 5.20 (1H, br.t, $J=7$ Hz –CH_2–$C\underline{H}$=C⟨), 5.50 (1H, br.d, $J=6.5$ Hz, C_{11a}–H), 6.53 (1H, s, C_{10}–H), 6.7—6.85 (2H, m, $C_{2,4}$–H), 7.08 (1H, s, C_7–H), 7.51 (1H, d, $J=8.3$ Hz, C_1–H). MS *m/e*: 408 (M^+), 366 (M^+-CH_2CO), 324 ($M^+-CH_2CO\times2$) base peak, 269 ($324-C_4H_7$), 147, 123, 43.

Sophoracoumestan A (III)——III was recrystallized from MeOH as colorless needles, mp over 300°, blue under UV light. TLC *Rf*: 0.66 (solv. 1). MS *m/e*: 334.0189 (M^+, Calcd for $C_{20}H_{14}O_5$: 334.0839), 319.0578 ($C_{19}H_{11}O_5$: 319.0604) base peak. UV λ^{EtOH}_{max} nm (log ε): 255 (4.47), 308 (3.86), 373 (4.46). IR ν^{KBr}_{max} cm^{-1}: 3320 (OH), 1710 (α-pyrone), 1630, 1610, 1500 (arom. C=C), 1370 (CH_3). PMR (Table II).

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References and Notes

1) Part XIII: M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.*, **26**, 3863 (1978) and references cited therein.
2) This work was reported at the Annual Meeting of the Pharmacognostic Society of Japan, Tokyo, November, 1979.
3) *a*) E. Wong, The isoflavonoids in "The Flavonoids," edited by J.B. Harborne, T.J. Mabry, and H. Mabry, Chapman and Hall, London, 1975, p. 759; *b*) *Idem*, *ibid.*, p. 774.
4) M. Martin and P.M. Dewick, *Tetrahedron Lett.*, **1978**, 2341; P.M. Dewick and M. Martin, *Phytochemistry*, **18**, 591, 597 (1979).
5) G.D. Monache, F.D. Monache, and G.B. Marini-Bettolo, *Gazz. Chim. Ital.*, **107**, 189 (1977).
6) Monache *et al.* have reported PMR signals of dicycloisosophoranone A[5] at δ 2.60 (A-ring) and 2.70 (B-ring) in CCl_4 and our PMR spectral measurement gave signals at δ 2.58 (A-ring) and 2.84 (B-ring) in $CDCl_3$.
7) M. Kaneda, T. Saitoh, Y. Iitaka, and S. Shibata, *Chem. Pharm. Bull.*, **21**, 1338 (1973).
8) T. Saitoh, H. Noguchi, and S. Shibata, *Chem. Pharm. Bull.*, **26**, 144 (1978).
9) K.G.R. Pachler and W.G.E. Underwood, *Tetrahedron*, **23**, 1817 (1967).
10) D.R. Perrin, C.P. Whittle, and T.J. Batterham, *Tetrahedron Lett.*, **1972**, 1673.
11) N.W. Preston, *Phytochemistry*, **16**, 2044 (1977).
12) C.v.d.M. Brink, J.P. Engelbrecht, and D.E. Graham, *Journal of the South African Chemical Institute*, 23, 24 (1970).
13) G.K. Gupta, K.L. Dhar, and C.K. Atal, *Phytochemistry*, **16**, 403 (1977).