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Studies on the Constituents of *Sophora* Species. XIII.[1] Constituents of the Aerial Parts of *Sophora tomentosa* L. (2)

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Two new flavonoid compounds, named sophoraisoflavanone A (I), mp 178—180°, $C_{21}H_{22}O_6$, and sophoraflavanone B (II), mp 193—195°, $C_{20}H_{20}O_5$, together with sophoronol (IV), isosophoranone (V) and isobavachin (VI) were isolated from the aerial parts of *Sophora tomentosa* L. Besides them, a new phenolic compound (III), mp 108—110°, $C_{27}H_{44}O_4$, was also isolated. The structures of them were determined by chemical and spectroscopic studies.

Sophoraisoflavanone A (I) exhibited antifungal activity.

Keywords——*Sophora tomentosa* L.; Leguminosae; sophoraisoflavanone A; sophoraflavanone B; 1-octadecanoyl cafferate; sophoronol; isosophoranone; isobavachin; prenylflavonoid; antifungal activity

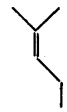
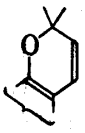
In the previous paper,[1] we reported the isolation and the structure elucidation of two new benzofuran derivatives, 2-(2′,4′-dihydroxyphenyl)-5,6-methylenedioxybenzofuran (VII) and 2-(2′-hydroxy-4′-methoxyphenyl)-5,6-methylenedioxybenzofuran (VIII) with a few known compounds as the constituents of the aerial parts of *Sophora tomentosa* L. In our further studying on the constituents of this plant, two new flavonoid compounds, named sophoraisoflavanone A (I), sophoraflavanone B (II), and a group of new phenolic compounds (III), together with sophoronol (IV), isosophoranone (V) and isobavachin (VI) have been isolated. The present paper deals with the structure elucidation and the antifungal activities of these compounds.

Sophoraisoflavanone A (I) was obtained as colorless needles, mp 178—180°, $[\alpha]_D^{22}$ −17.3° (EtOH), M^+=370.1435 (Calcd. for $C_{21}H_{22}O_6$: 370.1415), $C_{21}H_{22}O_6$, exhibiting negative Mg-HCl test, positive ferric chloride reaction and 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, 1600 cm^{-1}), and the ultraviolet (UV) spectrum (λ_{max}^{EtOH}=291, 330$_{(sh)}$ nm) suggested the presence of flavanone or isoflavanone skeleton in I.[3a] From the negative Mg-HCl test and the proton magnetic resonance (PMR) spectrum of I [$(CD_3)_2CO$] showing a complex multiplet (3H) at δ 4.4—4.6, attributed to the protons on the C-ring of an isoflavanone,[4] I was considered as the isoflavanone derivatives, which was also supported by ^{13}C-nuclear magnetic resonance (CMR) spectrum. That is to say, the signals at δ 70.7 (t) and 44.6 (d) (DMSO-d_6) were attributed to the carbons of C-2 and C-3 of isoflavanones, respectively.

Furthermore in the PMR spectrum of I, two signals at δ 1.68 (3H) and 1.78 (3H) for two vinyl methyl groups and a broad triplet at δ 5.30 (1H) due to vinylic protons split by methylene group, which was appeared at δ 3.39 (2H) as a doublet (J=6.4 Hz), suggested the presence of a γ,γ-dimethylallyl group. Besides them it shows singlet at δ 3.75 (3H, -OCH_3), singlet

1) Part XII: M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1274 (1978).
2) Location: *Keyakidai 1-1, Sakado, Saitama, 350-02, Japan.*
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*) B.A. Bohm, Flavanones and dihydroflavonols in *ibid.*, p. 594.
4) *a*) G.D. Monache, F.D. Monache, and G.B. Marini-Bettolo, *Gazz. Chim. Ital.*, **107**, 189 (1977); *b*) R.S. Bulden, J.A. Bailey, and G.W. Dawson, *Tetrahedron Lett.*, **1972**, 4175.

Table I. CMR Spectra Data (δ: ppm from TMS in DMSO d_6)

Carbon	I	II	IV	V	VI	Naringenin
2	70.7(t)	78.3	75.5(d)	70.8(t)	78.8	78.8(d)
3	44.6(d)	42.0	73.4(d)	44.7(d)	43.0	42.4(t)
4	198.0(s)	197.1	195.2(s)	198.1(s)	191.0	196.4(s)
4a	102.4(s)	—	100.5(s)	102.3(s)	115.1[a]	102.1(s)
5	164.2(s)	161.6	165.0(s)	161.1(s)[a]	125.4	163.7(s)
6	96.1(d)	107.1	96.3(d)	108.0(s)	113.8[a]	96.3(d)
7	167.0(s)	164.7	166.9(s)	164.6(s)	162.1	166.9(s)
8	95.0(d)	95.4	95.1(d)	94.5(d)	109.8[a]	95.4(d)
8a	163.5(s)	160.1	162.8(s)	161.4(s)[a]	160.9	163.1(s)
1′	121.3(s)	129.5	123.9(s)	121.4(s)	129.8	129.1(s)
2′	156.3(s)	128.3	154.2(s)[a]	156.4(s)	128.2	128.5(d)
3′	118.9(s)	115.4	113.8(s)	119.1(s)	115.3	115.6(d)
4′	157.9(s)	157.9	153.4(s)[a]	157.9(s)	157.7	157.9(s)
5′	111.4(d)	115.4	111.2(d)	111.4(d)	115.3	115.6(d)
6′	127.3(d)	128.3	128.1(d)	127.3(d)	128.2	128.5(d)
	17.7(q)	17.5		17.7(q)×2	17.6	
	23.0(t)	—		20.7(t)	21.7	
	25.5(q)	25.5		23.2(t)	25.5	
	123.5(d)	122.9		25.5(q)×2	122.4	
	130.5(s)	130.5		122.9(d)	130.8	
				123.6(d)		
				130.5(s)×2		
			26.6(q)			
			27.7(q)			
			74.3(s)			
			117.4(d)			
			130.6(d)			
$-OCH_3$	61.7(q)		62.1(q)	61.8(q)		

a) Signals may be interchanged.

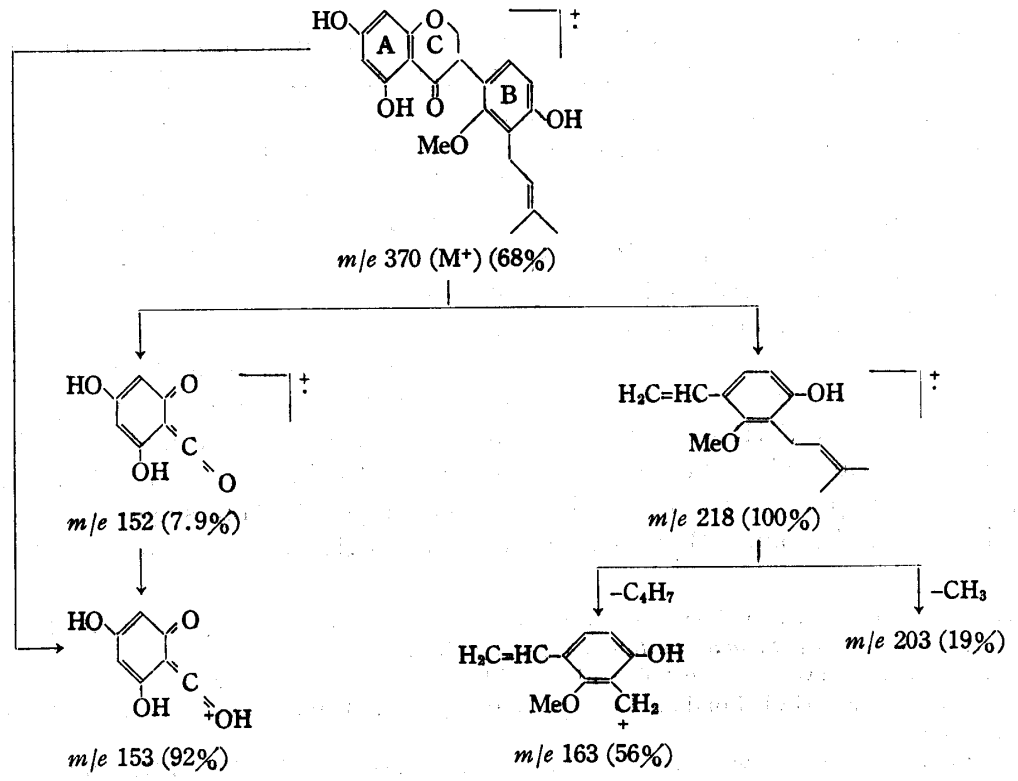


Chart 1. Fragmentation in MS of Sophoraisoflavanone A (I)

at δ 5.98 (2H),[5] a pair of doublets of AB type protons at δ 6.64 and 6.88 (1H, J=8.4 Hz), and three hydroxyl groups, one of them was chelated hydroxyl proton at δ 12.4 (disappeared by the addition of D_2O).

On methylation with diazomethane, I gave tetramethyl ether (Ia), mp 135—137°, $C_{24}H_{28}O_6$, whose PMR spectrum showed the signals due to four methoxyl groups at δ 3.72 (3H), 3.81 (6H) and 3.88 (3H), and therefore I possesses three hydroxyl groups on aromatic ring.

The substitution pattern of I was deduced from mass spectrum (MS) and CMR spectrum data. The MS of I showed retro-Diels-Alder cleavage giving rise to m/e 152 (7.9%), 153 (92%) and 218 (100%) as shown in Chart 1.

In view of the PMR spectrum data, the fragment at m/e 152 and 153 must incorporate A-ring and possesses two hydroxyl groups. Since CMR spectrum (DMSO-d_6) of I showed signals at δ 95.0 (d, C-8) and 96.1 (d, C-6) and UV absorption maxima of I was shifted bathochromically by 20—40 nm in the presence of sodium acetate and aluminum chloride, the hydroxyl groups were located at C-5 and C-7.

The fragment at m/e 218 must incorporate B-ring. This fragment loses CH_3 and C_4H_7 to yield m/e 203 (19%) and 163 (50%) respectively.

Therefore B-ring contains the methoxyl and γ,γ-dimethylallyl groups.

The above results can be summarized by the following partial formula for sophoraisoflavanone A (Fig. 1).

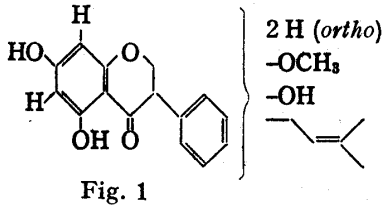


Fig. 1

The B-ring substitution pattern was determined as follows. On refluxing a solution of I in methanolic hydrochloric acid, the γ,γ-dimethylallyl side chain was cyclized with the neighbouring hydroxyl group to form only one chromane (Ib). Ib has the composition of $C_{21}H_{22}O_6$ which gave the PMR spectrum ($CDCl_3$) showing the presence of two tertiary methyls at δ 1.38 (s, 6H) and two methylene groups of 2,2-dimethylchromane ring at δ 1.82 (2H, br. t, J=6.2 Hz) and 2.84 (2H, br. t, J=6.2 Hz).[6] From these findings, there are six possibilities for the substitution patterns of I in B-ring.

Finally, the chemical proof was attempted in the following way. On oxidation with hydrogen peroxide in alkaline solution, Ib gave two products. The main oxidation product (Ic): M^+=280.1323 (Calcd. for $C_{15}H_{20}O_5$: 280.1310), $C_{15}H_{20}O_5$, comes from B-ring, keeping methoxyl group [PMR: δ 3.87 (3H, s)], one chromane ring [δ 1.36 (6H, s), 1.81 (2H, br. t,

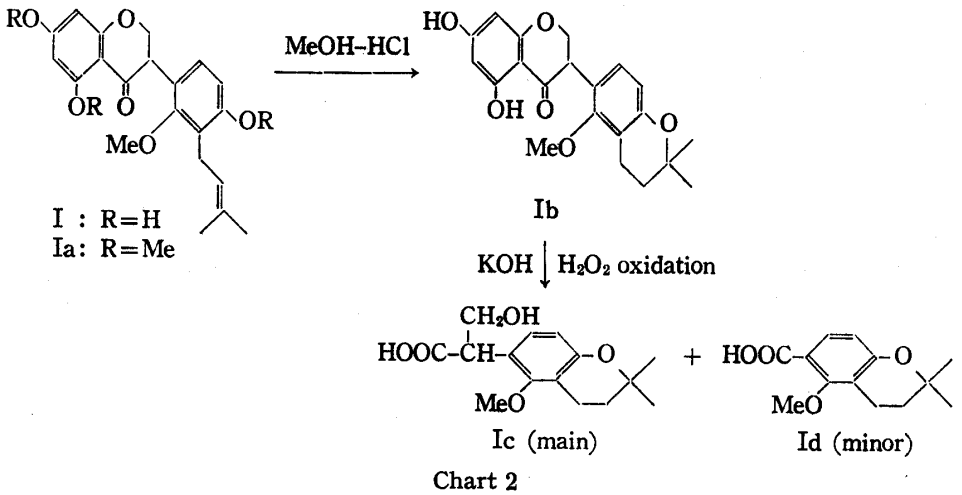


Chart 2

5) The signals were split to a pair of doublets at δ 5.91 (1H, d, J=2 Hz) and 6.08 (1H, d, J=2 Hz) in trimethylsilyl ether of I.

6) The physical data (UV, PMR and MS) of Ib were almost the same to that of dihydrosophoronol.[4a]

J=7 Hz), 2.84 (2H, br. t, J=7 Hz)] and two *ortho* aromatic protons [δ 6.67 (1H, d, J=8.7 Hz), 7.12 (1H, d, J=8.7 Hz)].

It contains an alcoholic function together with the acidic one (PMR, IR), and the losses of COOH and CH_2OH are observed in MS. The minor product (Id): mp 115—116°, $C_{13}H_{16}O_4$=236 also comes from B-ring. The spectrum data of this compound were in good agreement with those of 5-methoxy-2,2-dimethylchromane-6-carboxylic acid derived from sophoronol.[7] The structure of Ic can be assigned to the hydroxy-acid of the same aromatic skeleton of Id. Accordingly, the structure of Ic was established to be 3-hydroxy-2-(5-methoxy-2,2-dimethyl-6-chromanyl) propanoic acid.

In conclusion, the structure of sophoraisoflavanone A have been established as I.

The specific optical rotation of I had a minus (—) sign and this is the 3rd example of optical active natural isoflavanones.[8] Further work on the stereochemistry of these compounds are in progress.

Sophoraflavanone B (II) was obtained as colorless needles, mp 193—195°, $[\alpha]_D^{22}$ —25° (EtOH), M^+=340.1306 (Calcd. for $C_{20}H_{20}O_5$: 340.1309), $C_{20}H_{20}O_5$, exhibiting positive ferric chloride reaction and Gibbs reaction. It gave the absorption bands of hydroxyl and carbonyl groups in the IR spectrum. The UV spectrum indicated characteristic of 7-hydroxyflavanone series giving the absorption maxima at 339 nm in the presence of sodium hydroxide.[10] The PMR spectrum of II revealed the presence of a γ,γ-dimethylallyl group [δ 1.61 (6H, s), 3.22 (2H, br. d, J=7.9 Hz), 5.20 (1H, br. t, J=7.9 Hz)], C-2 proton [δ 5.45 (1H, q, J=12.1 Hz, 3.5 Hz)], C-3 protons [δ 2.60—3.13, (2H, m)], five aromatic protons [δ 6.03 (1H, s), 6.92 (2H, d, J=8.8 Hz), 7.42 (2H, d, J=8.8 Hz)], and three hydroxyl groups, one of them was chelated hydroxyl proton at δ 12.15 (disappeared by the addition of D_2O). In the MS of II, the retro-Diels-Alder cleavage of the molecular ion (M^+=340) led to major fragments at *m/e* 220 [($C_{12}H_{12}O_4^{\cdot+}$), A-ring] and *m/e* 120 [($C_8H_8O^{\cdot+}$), B-ring]. UV shifts after the addition of sodium acetate, aluminum chloride and sodium ethoxide suggested that three hydroxyl groups were located at C-7, C-5 and C-4′ respectively.

The similarity of the chemical shifts of H-6 and H-8 in 5,7-dihydroxyflavanone derivatives allows two possibilities for the attachment of the γ,γ-dimethylallyl group in A-ring at C-6 or C-8.

Wenkert *et al.*[11] have reported the ^{13}C chemical shifts of C-6 and C-8 were appeared at δ 96.3 and 95.4 in the CMR spectrum of naringenin, respectively. CMR spectrum of II showed at δ 107.1 (C-6) and 95.4 (C-8). Consequently, γ,γ-dimethylallyl group was shown to be located at C-6, which was also supported by the blue coloration with Gibbs reaction.

Therefore, the structure of sophoraflavanone B was represented by II.[12]

Since the specific optical rotation of II had a minus (—) sign, as other natural flavanones,[3b] II most probably has an (*S*)-configuration at C-2.

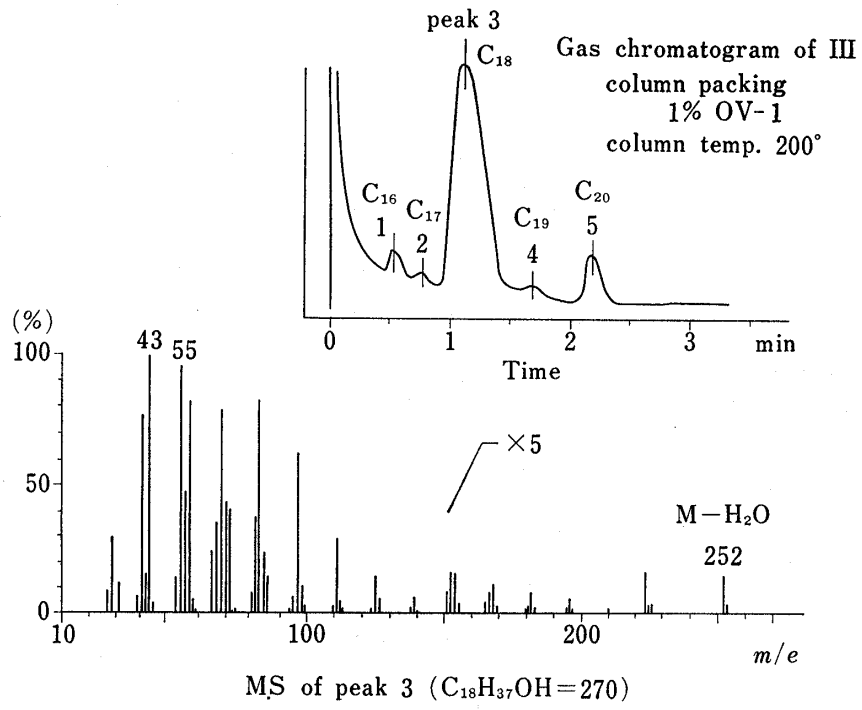
III was obtained as colorless needles, mp 108—110°, M^+=432.3217 (Calcd. for $C_{27}H_{44}O_4$: 432.3237), $C_{27}H_{44}O_4$, exhibited positive ferric chloride reaction and *ortho*-diphenol reaction. The IR spectrum suggested the presence of hydroxyl, α,β-unsaturated ester, aromatic ring and polymethylene group, and the UV spectrum of III gave indistinguishable data from those of caffeic acid. Since the PMR spectrum showed the presence of a primary methyl

7) F.D. Monache, G.D. Monache, and G.B. Marini-Bettolo, *Gazz. Chim. Itali.*, **106**, 935 (1976).
8) Only two optical active isoflavanone derivatives, sophorol[9] from *S. japonica* and isosophoranone[4a] from *S. tomentosa*, have been isolated so far.
9) H. Suginome, *J. Org. Chem.*, **24**, 1655 (1959).
10) Y. Tomita, "Zikken Kagaku Koza (Supplementary Volume)," Vol. 5, ed. by The Chemical Society of Japan, Maruzen Co. Ltd., Tokyo, 1966, pp. 940—942.
11) E. Wenkert and H.E. Gottlieb, *Phytochemistry*, **16**, 1811 (1977).
12) Recently, Ashish Nagar *et al.* have reported the synthesis of 6-C-prenyl naringenin (*Tetrahedron Lett.*, **1978**, 2031).

at δ 0.85 (3H, t, J=4.5 Hz), polymethylene group at δ 1.23 (*ca.* 32H, s), -COOC$\underline{H_2}$CH$_2$ at δ 4.1 (2H, t, J=6 Hz), indicating that the *n*-alkyl ester functional group must be presented in III. And in the PMR spectrum of III, a multiplet at δ 6.7—7.1 (3H, m) showed the presence of ABX type protons on aromatic ring, a pair of doublets (J=16 Hz) at δ 6.24 (1H) and 7.46 was assigned the H_α and H_β of Ar-CH$_\beta$=CH$_\alpha$-COOR, *trans*, respectively.

From the above data, III was assumed the *trans*-caffeic acid stearyl ester (1-octadecanoyl cafferate).

Whereas, III was hydrolysed with alkali to give caffeic acid and an aliphatic alcohol, $C_nH_{2n+1}OH$. GC-MS of the alcohol fraction established the chain-length to be constituted of C_{16}, C_{17}, C_{18} (main), C_{19} and C_{20} (Fig. 2).



MS of peak 3 ($C_{18}H_{37}OH$=270)

Fig. 2. GC-MS of III

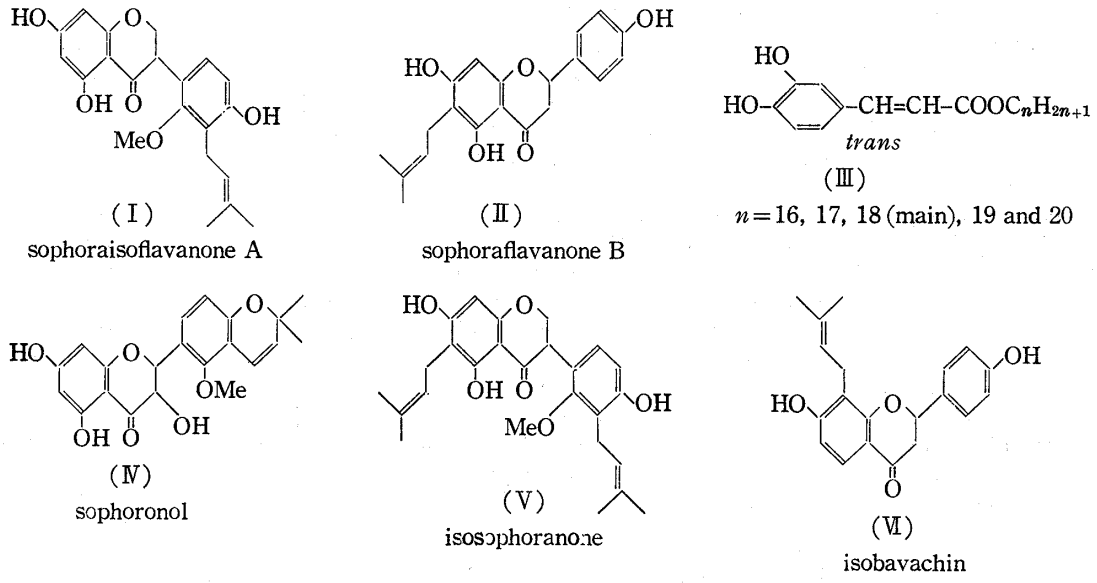


Fig. 3

Consequently, III was formulated as Fig. 3.

M. Komatsu, one of the authors, has already reported *trans*-caffeic acid docosyl ester. $C_{31}H_{52}O_4$ from *S. subprostrata*,[13] and III was an additional one of this series. Furthermore, sophoronol (IV),[7] isosophoranone (V),[4a] and isobavachin (VI),[14] were also isolated.

The antifungal activities of I, VII, VIIa, VIIb, and *l*-maackiain were shown in Table II.

Table II. Antifungal Activities of I, VII, VIIa, VIIb and *l*-Maackiain

	I	VII	VIIa	VIIb	*l*-Maackiain	Erythromycin	Cetyltrimethyl	Decanium chloride
Staphylococcus aureus 209 P	18.5	10	±	0	0	29		
Escherichia coli NIHJ	9.5	8.5	0	0	0	17		
Bacillus subtilis PCI 219	21	13	0	0	0	33		
Aspergillus niger NHL 5088	±	±	0	0	0		22	18
Aspergillus fumigatus IAM 2400	±	9	0	0	±		18	22
Penicillium citrinum IAM 7003	13	11	0	±	±		15	18
Candida albicans Yu 1200	9.5	9	0	0	0		13	15
Saccharomyces sake	±	9	0	0	0		±	10

Inhibitory circle (diameter, mm) by Disk methods.
Concentration: 2 mg/ml (control: 1 mg/ml).
VIIa: diacetate of compound VII, VIIb: dimethyl ether of compound VII.

I and VII exhibited antifungal activities. These minimum inhibitory concentration (MIC) are under investigation.

Experimental

All melting points were determined by a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. IR and UV spectra were recorded on a Nihon Bunko Model IRA-1 and UVIDIC-1 spectrometer, respectively. PMR and CMR spectra were measured at 100 MHz with a JNM-PS-100 spectrometer and 25 MHz with a JNM-PFT-100 NMR spectrometer, respectively, and chemical shifts are given on δ (ppm) scale with tetramethylsilane as the 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.

GC-MS was run on a Shimadzu LKB-9000 using column (1.0 m × 3 mmϕ) packed with 1% OV-1. Column chromatography was carried out with Wakogel C-200 and Polyamide 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 spraying 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 aerial parts of *Sophora tomentosa* L., which were collected in Republic of China in 1976, was extracted three times with boiling MeOH. The ether-soluble part (20 g) of the MeOH extract was subjected to rough separation with polyamide column chromatography into about 10 fractions. Each fraction was carefully rechromatographed on silica gel using benzene–AcOEt (with increasing concentrations of AcOEt from 0 to 50%) as the solvents. Thus, 2-(2′,4′-dihydroxyphenyl)-5,6-methylenedioxybenzofuran, 2-(2′-hydroxy-4′-methoxyphenyl)-5,6-methylenedioxybenzofuran, formononetin, isoliquiritigenin, *l*-maackiain, medicagol, stigmasterol were isolated.[1] Furthermore, 6 compounds (I—VI) were isolated, VI (14 mg), II (15 mg), IV (6.5 g), V (90 mg), I (185 mg), III (10 mg), respectively.

Sophoraisoflavanone A (I)——I was recrystallized from benzene as colorless needles, mp 178—180°, $[\alpha]_D^{22}$ −17.3° (c=0.26, EtOH), brown under UV light, greenish brown to $FeCl_3$, dark blue to Gibbs reaction. TLC *Rf*: 0.67 (benzene–AcOEt=1:1) (solv. 1). *Anal.* Calcd. for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99. Found:

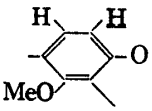
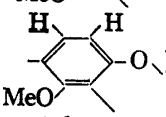
13) M. Komatsu, T. Tomimori, K. Hatayama, and Y. Makiguchi, *Yakugaku Zasshi*, **90**, 459 (1970).
14) V.K. Bhalla, U.R. Nayak, and S. Dev, *Tetrahedron Lett.*, **1968**, 2401.

C, 68.56; H, 6.17. MS *m/e*: 370.1435 (M^+, Calcd. for $C_{21}H_{22}O_6$: 370.1415), 218.1288 ($C_{14}H_{18}O_2$: 218.1305) base peak, 203.1064 ($C_{13}H_{15}O_2$: 203.1071), 163.0763 ($C_{10}H_{11}O_2$: 163.0758), 153.0186 ($C_7H_5O_4$: 153.0186). UV λ_{max}^{EtOH} nm (log ε): 291 (4.43), 330 (sh) (4.02). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm (log ε): 312 (4.43), 380 (3.72). UV $\lambda_{max}^{EtOH+NaOAc}$ nm (log ε): 302 (sh) (4.23), 331 (4.49). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1640 (C=O), 1610, 1600 (arom. C=C), 1390 (CH_3). PMR [$(CD_3)_2CO$]: 1.68, 1.78 (each 3H, each s, $=C(CH_3)_2$), 3.39 (2H, br. d, J=6.4 Hz, Ar–CH_2–CH=), 3.75 (3H, s, $-OCH_3$), 4.4—4.6 (3H, m, C_2–H_2, C_3–H), 5.30 (1H, br. t, J=6.4 Hz, $-CH_2-CH=C<$), 5.98 (2H, s, $C_{6,8}$–H), 6.64 (1H, d, J=8.4 Hz, C_5'–H), 6.88 (1H, d, J=8.4 Hz, C_6'–H), 8.6, 9.6 (each 1H, br, OH×2; disappeared by the addition of D_2O), 12.4 (1H, s, C_5–OH; disappeared by the addition of D_2O).

Methylation of I (Ia)——To a solution of I in MeOH, an ether solution of CH_2N_2 was added at 0°. After standing at room temp. for 24 hr, the solvent was removed and residue was recrystallized from MeOH as colorless prisms, mp 135—137°, no color to $FeCl_3$. MS *m/e*: 412.1896 (M^+, Calcd. for $C_{24}H_{28}O_6$: 412.1884), 232.1455 ($C_{15}H_{20}O_2$: 232.1461) base peak, 217.1208 ($C_{14}H_{17}O_2$: 217.1227), 181.0498 ($C_9H_9O_4$: 181.0499). UV λ_{max}^{EtOH} nm: 284, 320 (sh). IR ν_{max}^{KBr} cm^{-1}: 2920, 1385 (CH_3), 1675 (C=O), 1600, 1575 (arom. C=C). PMR [$(CD_3)_2CO$]: 1.66, 1.77 (each 3H, each s, $=C(CH_3)_2$), 3.35 (2H, br. d, J=6.7 Hz, Ar–CH_2–CH=), 3.72 (3H, s, $-OCH_3$), 3.81 (6H, s, $-OCH_3\times2$), 3.88 (3H, s, $-OCH_3$), 4.15 (1H, q, J=9.2 Hz, 6.1 Hz, C_3–H), 4.45—4.55 (2H, m, C_2–H_2), 5.21 (1H, br. t, J=6.7 Hz, $-CH_2-CH=C<$), 6.15 (1H, d, J=2.1 Hz, C_6–H), 6.22 (1H, d, J=2.1 Hz, C_8–H), 6.70 (1H, d, J=8.7 Hz, C_5'–H), 6.97 (1H, d, J=8.7 Hz, C_6'–H).

Acid-catalized Cyclization of I (Formation of Ib)——A mixture of I (84 mg), conc.HCl (5 ml), and MeOH (20 ml) was refluxed for 2 hr. The reaction mixture was diluted with water and extracted with ether. The ether extract was evaporated *in vacuo*, and purified by chromatography on silica gel with benzene to give Ib as an oil (68 mg). MS *m/e*: 370.1407 (M^+, Calcd. for $C_{21}H_{22}O_6$: 370.1415), 218.1301 ($C_{14}H_{18}O_2$: 218.1305) base peak, 203.1057 ($C_{13}H_{15}O_2$: 203.1071), 163.0733 ($C_{10}H_{11}O_2$: 163.0758), 162.0654 ($C_{10}H_{10}O_2$: 162.0679), 153.0182 ($C_7H_5O_4$: 153.0187). UV λ_{max}^{EtOH} nm: 292, 332 (sh). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm: 303, 385. UV $\lambda_{max}^{EtOH+NaOAc}$ nm: 330. IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1640 (C=O), 1600, 1480 (arom. C=C). PMR ($CDCl_3$): 1.38 (6H, s, $-O-C(CH_3)_2$), 1.82 (2H, br. t, J=6.2 Hz, $-CH_2-CH_2-O>C<$), 2.84 (2H, br. t, J=6.2 Hz, Ar–CH_2–CH_2–), 3.84 (3H, s, $-OCH_3$), 4.2—4.5 (3H, m, C_2–H_2, C_3–H), 5.95—6.20 (2H, m, $C_{6,8}$–H), 6.69 (1H, d, J=8.7 Hz, C_5'–H), 6.97 (1H, d, J=8.7 Hz, C_6'–H), 12.11 (1H, s, C_5–OH; disappeared by the addition of D_2O).

Hydrogen Peroxide Cleavage of Ib (Formation of Ic and Id)——30% H_2O_2 (0.5 ml) was added dropwise (30 min) with stirring, to Ib (17 mg) in 25% aqueous KOH (1 ml). The solution was maintained for 1 hr at 50° and then acidified with dil. HCl. The reaction mixture was extracted with AcOEt. The AcOEt extract was purified on a silica gel column chromatography (using benzene as the solvent), afforded two products: one (Ic) is a main product, and the other (Id) is a minor product.

Compound Ic [3-Hydroxy-2-(5-methoxy-2,2-dimethyl-6-chromanyl)propanoic Acid]——Ic was obtained as an oily product. MS *m/e*: 280.1323 (M^+, Calcd. for $C_{15}H_{20}O_5$: 280.1310) (48.8%), 249.1123 ($C_{14}H_{17}O_4$: 249.1125) (100%), 235 (M^+—COOH) (16.3%),* 225.0772 ($C_{11}H_{13}O_5$: 225.0762) (6.4%), 218.1298 ($C_{14}H_{18}O_2$: 218.1305) (21.2%), 205.1202 ($C_{13}H_{17}O_2$: 205.1227) (10.4%), 193.0487 ($C_{10}H_9O_4$: 193.0499) (25.1%), 179.0654 ($C_{10}H_{11}O_3$: 179.0707) (21.0%), 163 ($C_{10}H_9O_4$–OCH_2) (18.3%),* 149.0435 ($C_5H_9O_5$: 149.0449) (25.0%). [*The data were given by nominal MS]. UV λ_{max}^{EtOH} nm: 279. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3525, 1700, 1605, 1580, 1480, 1205, 1070. PMR ($CDCl_3$): 1.36 (6H, s, $-O-C(CH_3)_2$), 1.81 (2H, br. t, J=7 Hz, $-CH_2-CH_2-O>C$), 2.84 (2H, br. t, J=7 Hz, Ar–CH_2–CH_2–), 3.87 (3H, s, $-OCH_3$), 3.9—4.4 (3H, m, –CH–CH_2–), 6.67 (1H, d, J=8.7 Hz, ), 7.00 (2H, br, –COOH+OH; disappeared by the addition of D_2O), 7.12 (1H, d, J=8.7 Hz, ).

Compound Id——Recrystallization from a mixture of benzene–hexane gave colorless crystal, mp 115—116°. MS *m/e*: 236 (M^+, $C_{13}H_{16}O_4$), 221, 218, 203, 181, 151 base peak. This was identified by the direct comparison with 5-methoxy-2,2-dimethylchromane-6-carboxylic acid derived from sophoronol.

Sophoraflavanone B (II)——Recrystallization from a mixture of benzene–AcOEt gave colorless needles, mp 193—195° with foregoing wetting at about 150—155°, $[\alpha]_D^{22}$ −25° (c=0.1, EtOH), orange brown under UV light, greenish brown to $FeCl_3$, purple to Gibbs reaction. TLC *Rf*: 0.58 (solv. 1). MS *m/e*: 340.1306 (M^+, Calcd. for $C_{20}H_{20}O_5$: 340.1309) base peak, 325.1094 ($C_{19}H_{17}O_5$, 325.1074), 297.0767 ($C_{17}H_{13}O_5$: 297.0762), 285.0780 ($C_{16}H_{13}O_5$: 285.0762), 220.0735 ($C_{12}H_{12}O_4$: 220.0735), 205.0503 ($C_{11}H_9O_4$: 205.0500), 192.0777 ($C_{11}H_{12}O_3$: 192.0785), 177.0559 ($C_{10}H_9O_3$: 177.0551), 165.0187 ($C_8H_5O_4$: 165.0187), 120.0595 (C_8H_8O: 120.0574). UV λ_{max}^{EtOH} nm (log ε): 297 (4.51). UV $\lambda_{max}^{EtOH+EtONa}$ nm (log ε): 249 (4.77), 338 (4.77). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm (log ε): 314 (4.50), 395 (3.74). UV $\lambda_{max}^{EtOH+NaOAc}$ nm (log ε): 299 (sh) (4.38), 340 (4.47). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 339 (4.76). IR ν_{max}^{KBr} cm^{-1}: 3360 (OH), 1630 (C=O), 1600, 1520 (arom. C=C), 1380 (CH_3). PMR [$(CD_3)_2CO$]: 1.61

(6H, s, $=\langle^{CH_3}_{CH_3}$), 2.60—3.13 (2H, m, C_3–H_2), 3.22 (2H, br. d, J=7.9 Hz, Ar–CH_2–CH=), 5.20 (1H, br. t, J=7.9 Hz, –CH_2–CH=C$\langle$), 5.45 (1H, q, J=12.1 Hz, 3.5 Hz, C_2–H), 6.03 (1H, s, C_8–H), 6.92 (2H, d, J=8.8 Hz, $C_{3',5'}$–H), 7.42 (2H, d, J=8.8 Hz, $C_{2',6'}$–H), 8.5—11.0 (2H, br, OH×2; disappeared by the addition of D_2O), 12.15 (1H, s, C_5–OH; disappeared by the addition of D_2O).

Compound III——Recrystallization from MeOH gave colorless needles, mp 108—110°, dark blue under UV light, $FeCl_3$ (+), $SrCl_2$–NH_3 (+). TLC *Rf*: 0.62 (Solv. 1). MS *m/e*: 432.3217 (M^+, Calcd. for $C_{27}H_{44}O_4$: 432.3237), 180.0421 ($C_9H_8O_4$: 180.0421) base peak, 163.0396 ($C_9H_7O_3$: 163.0395). UV λ_{max}^{EtOH} nm (log ε): 248 (4.11), 301 (sh) (4.03), 332 (4.13). IR ν_{max}^{KBr} cm^{-1}: 3480, 3300 (OH), 2920, 2840, 1480, 1460 (CH), 1690, 1290, 1180 (conj. ester), 1610, 1540 (arom. C=C).

Hydrolysis of III——III was saponified with 5% KOH/90% MeOH for 3 hr at 60—70° with stirring under N_2 gas flow. The reaction mixture was partitioned between ether and H_2O. The ether layer was evaporated to dryness and the residue was recrystallized from EtOH to give colorless prisms, mp 55—60° which was identified stearyl alcohol ($C_{18}H_{37}OH$) with IR spectrum, but this was proved to be a mixture of $C_{16}H_{33}OH$ [MS *m/e*: 224=M–H_2O], $C_{17}H_{35}OH$ [MS *m/e*: 238=M–H_2O], $C_{18}H_{37}OH$ [MS *m/e*: 252=M–H_2O], $C_{19}H_{39}OH$ [MS *m/e*: 266=M–H_2O], and $C_{20}H_{41}OH$ [MS *m/e*: 280=M–H_2O] as a fractional part of 1.8: 0.7: 91.8: 0.5: 5.2% by GC-MS. The H_2O layer was neutralized with dil. HCl and extracted with EtOAc. After the evaporation of solvent the residue was recrystallized from MeOH–H_2O to give pale yellow powder, caffeic acid which was identified by direct comparison (TLC, UV, mp and IR) with an authentic sample.

Sophoronol (IV)——Recrystallization from a mixture of benzene–petroleum ether gave colorless powder, mp 101—103°, $[\alpha]_D^{22}$ +215° (c=1.0, pyridine), brown under UV light, greenish brown to $FeCl_3$, purple blue to Gibbs reaction. TLC *Rf*: 0.67 (solv. 1). MS *m/e*: 384.1239 (M^+, Calcd. for $C_{21}H_{20}O_7$: 384.1207). This was identified by the direct comparison (mixed mp, TLC, UV, IR, PMR and MS) with an authentic sample.[15]

Isosophoranone (V)——Recrystallization from a mixture of benzene–AcOEt gave pale yellow needles, mp 182—183°, $[\alpha]_D^{22}$ 0° (c=0.13, EtOH), brown under UV light, greenish brown to $FeCl_3$, purple blue to Gibbs reaction. TLC *Rf*: 0.68 (solv. 1). MS *m/e*: 438.2018 (M^+, Calcd. for $C_{26}H_{30}O_6$: 438.2040), 383.1480 ($C_{22}H_{23}O_6$: 383.1492), 221.0801 ($C_{12}H_{13}O_4$: 221.0812), 220.0737 ($C_{12}H_{12}O_4$: 220.0735), 218.1300 ($C_{14}H_{18}O_2$: 218.1305).

The spectral data (UV, IR and PMR) of V were very similar to that of isosophoranone but this was isolated as a racemate like other natural isoflavanones.

Isobavachin (VI)——Recrystallization from a mixture of MeOH–H_2O gave colorless needles, mp 200—202°, $[\alpha]_D^{22}$ −46° (c=0.13, EtOH), negative to $FeCl_3$ and Gibbs reaction. TLC *Rf*: 0.49 (solv. 1). MS *m/e*: 324.1363 (M^+, Calcd. for $C_{20}H_{20}O_4$: 324.1360) base peak, 269.0812 ($C_{16}H_{13}O_4$: 269.0813), 204.0791 ($C_{12}H_{12}O_3$: 204.0786), 149.0264 ($C_8H_5O_3$: 149.0238), 120.0567 (C_8H_8O: 120.0574). UV λ_{max}^{EtOH} nm: 286. UV $\lambda_{max}^{EtOH+NaOAc}$ nm: 288 (sh), 348. IR ν_{max}^{KBr} cm^{-1}: 3240 (OH), 1640 (C=O), 1600, 1520 (arom. C=C), 1390 (CH_3). PMR [$(CD_3)_2CO$]: 1.62 (6H, s, $=\langle^{CH_3}_{CH_3}$), 2.6—3.1 (2H, m, C_3–H_2), 3.33 (2H, br. d, J=7.4 Hz, Ar–CH_2–CH=), 5.22 (1H, br. t, J=7.4 Hz, –CH_2–CH=C$\langle$), 5.44 (1H, q, J=12.0 Hz, 3.6 Hz, C_2–H), 6.63 (1H, d, J=8.5 Hz, C_6–H), 6.90 (2H, d, J=8.6 Hz, $C_{3',5'}$–H), 7.41 (2H, d, J=8.6 Hz, $C_{2',6'}$–H), 7.59 (1H, d, J=8.5 Hz, C_5–H), 8.5—9.5 (2H, br, OH×2; disappeared by the addition of D_2O).

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15) The mp of sophoronol was reported at 158—160°,[7] but the data of which was gifted by Dr. F.D. Monache was 101—103°.