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

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A new 2-arylbenzofuran, named sophorafuran A (I), mp 145—146°C, $C_{16}H_{12}O_6$, and a new coumestan, named sophoracoumestan B (II), mp over 300°C, $C_{17}H_{10}O_7$, together with (−)-3-hydroxy-4-methoxy-8,9-methylenedioxypterocarpan (III) were isolated from the root of *Sophora franchetiana* Dunn (Leguminosae).

The structures of I and II were established to be 2-(2′,4′-dihydroxy-3′-methoxyphenyl)-5,6-methylenedioxybenzofuran and 3-hydroxy-4-methoxy-8,9-methylenedioxycoumestan, respectively, on the basis of chemical and spectral evidence.

Keywords——*Sophora franchetiana*; Leguminosae; sophorafuran A; sophoracoumestan B; benzofuran; coumestan; pterocarpan; flavonoid

In the previous paper,[1] we reported the isolation and the structure elucidation of three new flavonoids from the root of *Sophora franchetiana* Dunn.

In our further studies of this plant, a new 2-arylbenzofuran, named sophorafuran A (I), and a new coumestan, named sophoracoumestan B (II), together with (−)-3-hydroxy-4-methoxy-8,9-methylenedioxypterocarpan (III) have been isolated. This paper deals with the structural elucidation of these compounds.

Sophorafuran A (I) was obtained as colorless needles, mp 145—146 °C, M^+=300.0631 (Calcd for $C_{16}H_{12}O_6$: 300.0631), $C_{16}H_{12}O_6$, exhibiting positive ferric chloride reaction and Gibbs reaction, negative *ortho*-diphenol reaction [1. $SrCl_2$–NH_3, 2. $(NH_4)_6Mo_7O_{24}$[3]].

The infrared (IR) spectrum of I suggested the presence of hydroxyl groups (3400 cm^{-1}), an aromatic ring (1620, 1600, 1500 cm^{-1}) and a methylenedioxy group (1040, 940 cm^{-1}), and the ultraviolet (UV) spectrum suggested the 2-arylbenzofuran structure,[4] showing absorption maxima of 330 and 345 nm, which shift in alkali to 347 and 360 nm, respectively.

The proton magnetic resonance (PMR) spectrum of I shows one methoxyl group at δ 3.74 (3H, s), one methylenedioxy group at δ 6.02 (2H, s), two hydroxyl groups at δ 9.51 and 9.60 (disappeared on the addition of D_2O) and a pair of doublets of AB type protons on a *ortho*-coupled aromatic ring at δ 6.47 (1H, d, J=8.8 Hz) and 7.53 (1H, d, J=8.8 Hz), At the same time, the PMR spectrum exhibits three proton signals of olefinic or aromatic protons at δ 7.10 (2H, s) and 7.20 (1H, s).

On acetylation, I gave the diacetate (Ia), mp 146—147 °C, $C_{20}H_{16}O_8$, whose PMR spectrum showed signals due to two acetyl groups at δ 2.33 (3H, s) and 2.42 (3H, s); hence, I possesses two hydroxyl groups on an aromatic ring.

These data were similar to those of 2-(2′,4′-dihydroxyphenyl)-5,6-methylenedioxybenzofuran (IV)[4] except for one methoxyl group.

In a comparison of the ^{13}C-nuclear magnetic resonance (CMR) spectra of I and IV, I showed a methoxyl signal at δ 61.15 and showed upfield shifts of the signals of C-2′ (δ 157.16→150.40), C-4′ (δ 159.72→151.80) and C-6′ (δ 128.51→122.35), while the signal of C-3′ (δ 104.24→137.29)[5] showed a downfield shift (Fig. 1). From these results and the negative *ortho*-diphenol reaction of I, the methoxyl group should be located at C-3′.

Thus, I was determined to be 2-(2′,4′-dihydroxy-3′-methoxyphenyl)-5,6-methylenedioxybenzofuran.

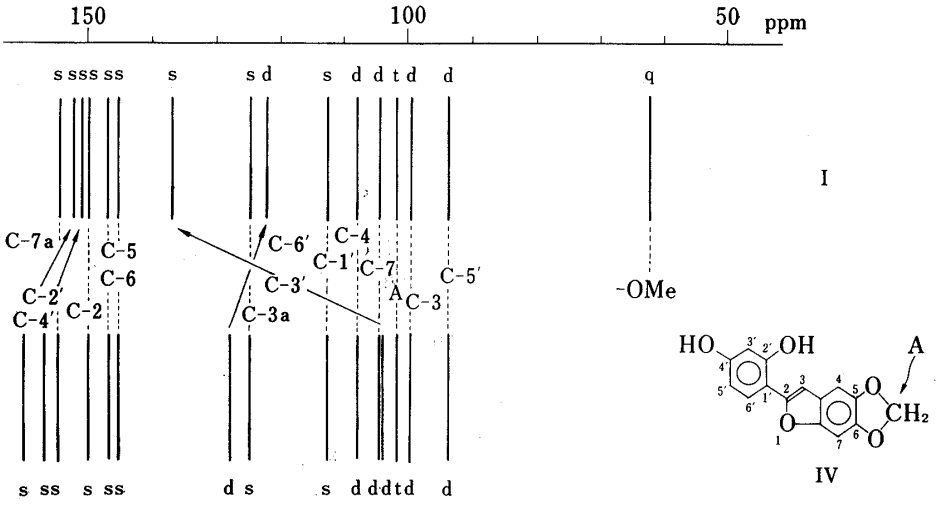


Fig. 1. CMR spectrum of I (in CD_3OD)

IV: 2-(2′, 4′-dihydroxyphenyl)-5,6-methylenedioxybenzofuran
off-resonance decoupling (SFORD). s, singlet; d, doublet; t, triplet; q, quartet

Sophoracoumestan B (II) was obtained as colorless needles, mp over 300 °C, M^+=326.0394 (Calcd for $C_{17}H_{10}O_7$: 326.0424) $C_{17}H_{10}O_7$, exhibiting negative Gibbs reaction.

It gave absorption bands of hydroxyl (3300 cm^{-1}) α-pyrone (1710 cm^{-1}), aromatic ring (1630, 1600, 1580 cm^{-1}) and methylenedioxy (1040, 940 cm^{-1}) moieties in the IR spectrum. The UV spectrum indicated a coumestan structure, with absorption maxima at 246, 275, $352_{(sh)}$ and 364 nm.

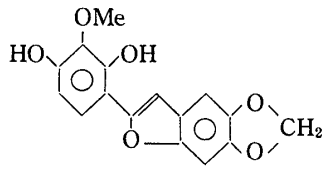
The PMR spectrum of II showed one methoxyl group at δ 3.89 (3H, s), one methylenedioxy group at δ 6.20 (2H, s) and a pair of doublets of AB type on the aromatic ring at δ 7.00 (1H, d, J=9 Hz, C_2–H) and 7.58 (1H, d, J=9 Hz, C_1–H), two protons signals at δ 7.29 (1H, s, C_{10}–H) and 7.50 (1H, s, C_7–H) and one hydroxyl group at δ 10.53 (1H, br. s,; disappeared on the addition of D_2O).

The substitution pattern of these functional groups was determined by comparison with the PMR spectrum of medicagol (3-hydroxy-8,9-methylenedioxycoumestan)[1] (Table I).

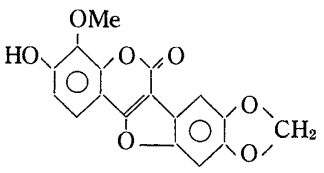
Table I. PMR Spectral Data for Coumestans (δ) ppm (in DMSO-d_6)

	1-H	2-H	4-H	7-H	8-H	9-H	10-H
II	7.58	7.00	3.89	7.50	6.20		7.29
	d, J=9 Hz	d, J=9 Hz	(-OMe)	s	($-OCH_2O-$)		s
Medicagol	7.82	6.9—7.0		7.48	6.20		7.30
	d, J=9 Hz	m		s	($-OCH_2O-$)		s

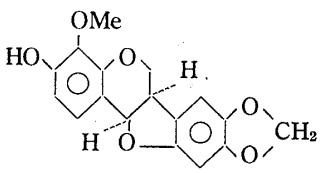
From these data and biogenetic considerations, the structure of sophoracoumestan B was concluded to be 3-hydroxy-4-methoxy-8,9-methylenedioxycoumestan.



sophorafuran A (I)



sophoracoumestan B (II)



(−)-3-hydroxy-4-methoxy-8,9-methylenedioxypterocarpan (III)

Fig. 2

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 JASCO IRA-1 spectrometer and a JASCO UVIDEC-1 spectrometer, respectively. PMR and CMR spectra were measured at 100 MHz with a JEOL JNM-PS-100 spectrometer and at 25 MHz with a JEOL 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 JEOL JMS-01SG-2 mass spectrometer with a direct inlet system. ORD and CD were taken with a JASCO J-20 spectrometer.

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 October, 1978, were extracted five times with boiling MeOH. The ether-soluble part (10 g) of the MeOH extract (32 g) was column chromatographed on silica gel (1.0 kg) by using benzene and benzene–AcOEt (9: 1—1: 1) as eluents and each fraction was checked by TLC (solv. benzene–AcOEt=1: 1). Sophoraisoflavanone B (123 mg), crude (−)-3-hydroxy-4-methoxy-8,9-methylenedioxypterocarpan (III), *l*-maackiain (40 mg), β-sitosterol (20 mg), crude I, crude II, sophorapterocarpan A (214 mg) and sophoracoumestan A (4 mg) were eluted in that order. Crude I to III were subjected to rechromatography on silica gel to yield I (72 mg), II (8 mg) and III (88 mg), respectively.

Sophorafuran A (I)——Recrystallization from benzene gave colorless needles, mp 145—146°C, greenish-brown to $FeCl_3$, dark blue to Gibbs reaction, *ortho*-diphenol reaction [1. $SrCl_2$–NH_3 (−), 2. $(NH_4)_6Mo_7O_{24}$ (−)]. MS *m/e*: 300.0631 (M^+, Calcd for $C_{16}H_{12}O_6$: 300.0631) base peak, 285.0365 ($C_{15}H_9O_6$: 285.0397), 201.0557 ($C_{12}H_9O_3$: 201.0552), 199.0376 ($C_{12}H_7O_3$: 199.0392), 171.0435 ($C_{11}H_7O_2$: 171.0445), 150.0354 ($C_8H_6O_3$: 150.0318). UV λ_{max}^{EtOH} nm (log ε): $245_{(sh)}$ (4.19) 288 (4.20), 330 (4.46), 345 (4.49). UV $\lambda_{max}^{EtOH+1\%KOH}$ nm (log ε): $252_{(sh)}$ (4.35), 294 (4.29), 347 (4.43), $360_{(sh)}$ (4.40). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1620, 1600, 1500 (arom. C=C), 1040, 940 (–OCH_2O–). PMR (DMSO-d_6): 3.74 (3H, s, –OCH_3), 6.02 (2H, s, –OCH_2O–), 6.47 (1H, d, J=8.8 Hz, C_5–H), 7.10 (2H, s, $C_{4,7}$–H), 7.20 (1H, s, C_3–H), 7.53 (1H, d, J=8.8 Hz, $C_{6'}$–H), 9.51, 9.60 (each 1H, each s, OH; disappeared on the addition of D_2O). CMR (CD_3OD): 61.15 (q, OCH_3), 94.00 (d, C-5′), 100.29 (d, C-3), 102.60 (t, –OCH_2O–), 105.22 (d, C-7), 109.12 (d, C-4), 112.36 (s, C-1′), 122.35 (d, C-6′), 124.91 (s, C-3a), 137.29 (s, C-3′), 146.07 (s, C-5 or C-6), 147.23 (s, C-6 or C-5), 149. 54 (s, C-2), 150.40 (s, C-2′), 151.80 (s, C-4′), 154.48 (s, C-7a).

Acetylation of I (Ia)——I was acetylated with Ac_2O and pyridine for 2 hr at 100°, and the reaction mixture was worked up as usual. Recrystallization from a mixture of $CHCl_3$–MeOH gave colorless needles, mp 146—147°, no color to $FeCl_3$. IR ν_{max}^{KBr} cm^{-1}: 1760, 1200 (ester), 1500, 1460 (arom. C=C), 1040, 940 (–OCH_2O–). PMR ($CDCl_3$): 2.33 (3H, s, $C_{4'}$–$OCOCH_3$), 2.42 (3H, s, $C_{2'}$–$OCOCH_3$), 3.85 (3H, s, $C_{3'}$–OCH_3), 6.00 (2H, s, –OCH_2O–), 6.90 (1H, d, J=1 Hz, C_7–H), 6.94 (1H, s, C_4–H), 6.98 (1H, d, J=1 Hz, C_3–H), 7.08 (1H, d, J=9 Hz, $C_{5'}$–H), 7.64 (1H, d, J=9 Hz, $C_{6'}$–H). MS *m/e*: 384 (M^+), 342 (M^+-CH_2CO), 300 ($M^+-CH_2CO\times2$) base peak, 43.

Sophoracoumestan B (II)——Recrystallization from MeOH gave colorless needles, mp over 300°C, blue under UV light, negative to Gibbs reaction. MS *m/e*: 326.0394 (M^+, Calcd for $C_{17}H_{10}O_7$: 326.0424) base peak, 311.0180 ($C_{16}H_7O_7$: 311.0190), 227.0317 ($C_{13}H_7O_4$: 227.0342), 199.0245 ($C_8H_7O_6$: 199.0243). UV λ_{max}^{EtOH} nm (log ε): 246 (4.34), 275 (4.07), $352_{(sh)}$ (4.47), 364 (4.50). IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1710 (α-pyrone), 1630, 1600, 1580 (arom. C=C), 1040, 940 (–OCH_2O–). PMR (Table I).

(−)-3-Hydroxy-4-methoxy-8,9-methylenedioxypterocarpan (III)[6]——Recrystallization from MeOH gave colorless needles, mp 159—161°C, negative to Gibbs reaction. MS *m/e*: 314.0823 (M^+, Calcd for $C_{17}H_{14}O_6$: 314.0791). ORD (c=0.01, EtOH): $[\phi]_{322}$ +620, $[\phi]_{284}$ −9420, $[\phi]_{274}$ −8480, $[\phi]_{256}$ −17700, $[\phi]_{240}$ −8160.

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References and Notes

1) Part XIV: M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.*, **29**, 532 (1981).
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5) 2-(2′,4′-dihydroxyphenyl)-5,6-methylenedioxybenzofuran (IV) CMR (CD_3OD): 94.00 (d, C-5′), 100.25 (d, C-3), 102.55 (t, $-OCH_2O-$), 104.24 (d, C-3′), 105.20 (d, C-7), 108.62 (d, C-4), 111.93 (s, C-1′), 124.97 (s, C-3a), 128.51 (d, C-6′), 146.06 (s, C-5 or C-6), 147.20 (s, C-6 or C-5), 149.78 (s, C-2), 154.77 (s, C-7a), 157.16 (s, C-2′), 159.72 (s, C-4′).
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