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Studies on the Constituents of *Sophora* Species. XVIII.[1] Constituents of the Root of *Sophora tomentosa* L. (3)[2]

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A new chromone, named sophorachromone A (I), mp 138—139 °C, $C_{19}H_{22}O_4$, and a new flavanone, named sophoraflavanone A (II), mp 144—145 °C, $C_{25}H_{28}O_5$, were isolated together with isosophoranone (III) from the root of *Sophora tomentosa* L. (Leguminosae). The structures of I and II were established to be 8-geranyl-5,7-dihydroxychromone and 6-geranyl-5,7,4′-trihydroxyflavanone, respectively, on the basis of chemical and spectral evidence.

Keywords——*Sophora tomentosa* L.; Leguminosae; sophorachromone A; sophoraflavanone A; chromone; flavanone; flavonoid; ^{13}C-NMR

In the previous papers,[2] we reported the isolation and structural elucidation of five new phenolics from *Sophora tomentosa* L. In our further studies of this plant, a new chromone, named sophorachromone A (I), and a new flavanone, named sophoraflavanone A (II), have been isolated, together with isosophoranone (III).[3] This paper deals with the structural elucidation of these compounds.

Sophorachromone A (I) was obtained as colorless plates, mp 138—139 °C, $M^+ = 314.1495$, $C_{19}H_{22}O_4$, exhibiting a positive ferric chloride reaction. The infrared (IR) spectrum of I suggested the presence of hydroxyl groups (3200—3400 cm^{-1}), aromatic rings (1620,

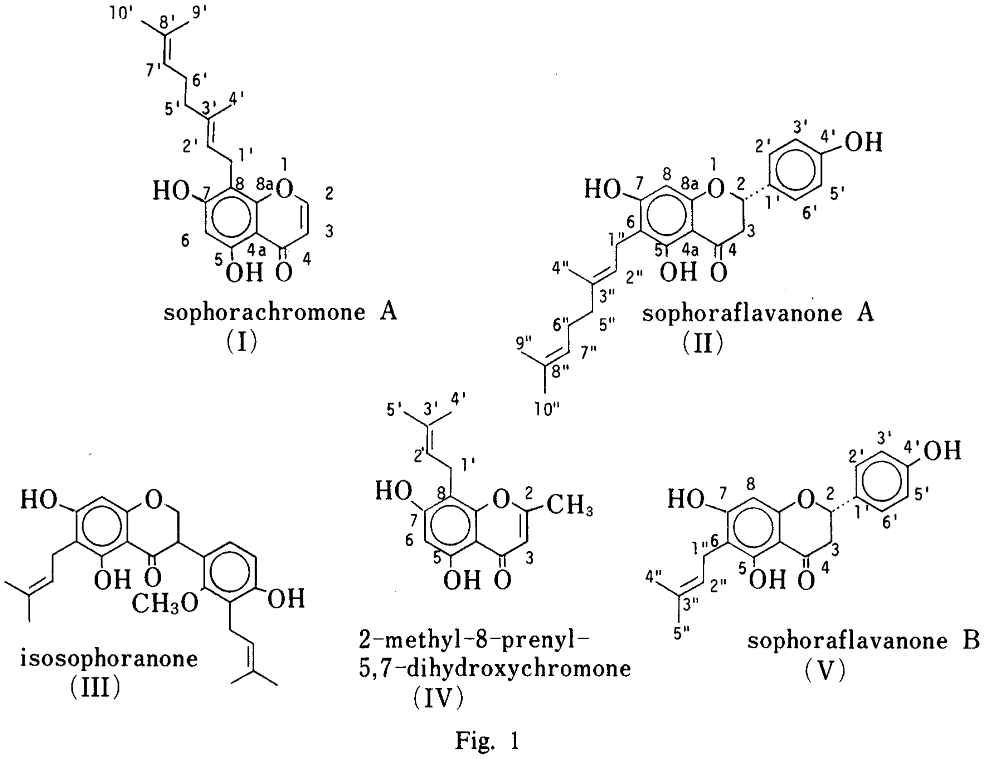
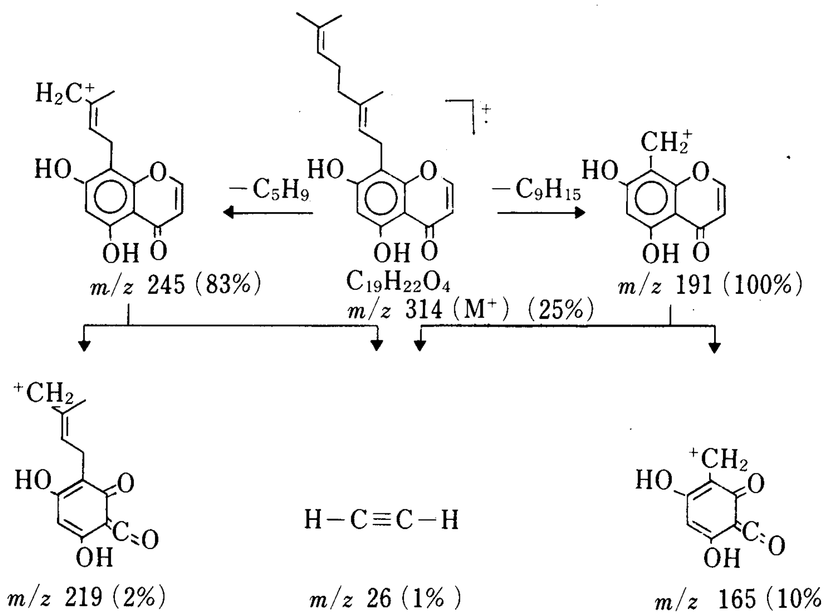


Fig. 1



MS fragmentation of I

Chart 1

1570 cm^{-1}) and a chelated carbonyl group (1650 cm^{-1}), and the ultraviolet (UV) spectrum suggested the chromone structure,[4a] showing absorption maxima at $218_{(sh)}$, 264 and 305 nm which shifted in the presence of aluminum chloride to 274 and 316 nm, respectively. Furthermore, I showed a blue color on the addition of hydrogen peroxide in alkaline solution.[4b] From these data, I was considered a 5,7-dihydroxychromone derivative.

The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of I (CD_3COCD_3) showed signals at δ 8.15 and δ 6.22, attributable to C_2-H and C_3-H of the chromone, respectively. It also indicated the presence of two hydroxyl groups [δ 9.6 and δ 12.7 (chelated with C_4 carbonyl), both of which disappeared on the addition of D_2O], one aromatic proton δ 6.35 (C_6 or C_8-H) and one geranyl (or neryl) group[5] [δ 1.54, 1.59, 1.80 ($C_{3'}$, $C_{8'}$-CH_3), δ 2.00 ($C_{5'}$, $C_{6'}$-H_2), δ 3.43 ($C_{1'}$-H_2) and δ 5.0—5.3 ($C_{2'}$, $C_{7'}$-H)]. The mass spectrum (MS) of I showed a fragment at m/z 191 $[C_{10}H_7O_4]^+$, which indicates the loss of 123 $[C_9H_{15}]^+$ mass units from the molecular ion, supporting the presence of a geranyl (or neryl) group in I (Chart 1). From these data, it is clear that there is one geranyl (or neryl) group in the 5,7-dihydroxychromone.

The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of I (CD_3COCD_3) showed signals at δ 158.1 (d) and δ 111.9 (d), attributable to C-2 and C-3 of the chromone ring. In comparison of the ^{13}C-NMR spectra of I and 2-methyl-8-prenyl-5,7-dihydroxychromone (IV), I showed signals of C-6 at δ 99.9 and C-8 at δ 108.2, while IV showed signals of C-6 at δ 99.2 and C-8 at δ 107.1 (Table 1). From these results, the geranyl (or neryl) group should be located at C-8. The possibility of a geranyl group is supported by the appearance in the ^{13}C-NMR spectrum of C-4′ at δ 16.7 and C-5′ at δ 40.9, respectively.[5,6] Thus, I was determined to be 8-geranyl-5,7-dihydroxychromone.

Sophoraflavanone A (II) was obtained as colorless needles, mp 144—145 °C, $[\alpha]_D^{22}$ −33° (EtOH), $M^+ = 408.1944$, $C_{25}H_{28}O_5$, exhibiting a positive ferric chloride reaction, Gibbs reaction and Mg-HCl test. It gave the absorption bands of hydroxyl groups (3400 cm^{-1}), aromatic rings (1620, 1520 cm^{-1}) and a chelated carbonyl group (1640 cm^{-1}) in the IR spectrum. The UV spectrum was characteristic of the 7-hydroxyflavanone series, giving an absorption maximum at 340 nm in the presence of sodium acetate.[4c]

The ^{1}H-NMR spectrum of II revealed the presence of a geranyl (or neryl) group [δ 1.56 (3H), δ 1.62 (6H), $C_{3''}$, $C_{8''}$-CH_3; δ 1.97 ($C_{5''}$, $C_{6''}$-H_2); δ 3.24 ($C_{1''}$-H_2) and δ 5.0—5.3 ($C_{2''}$,

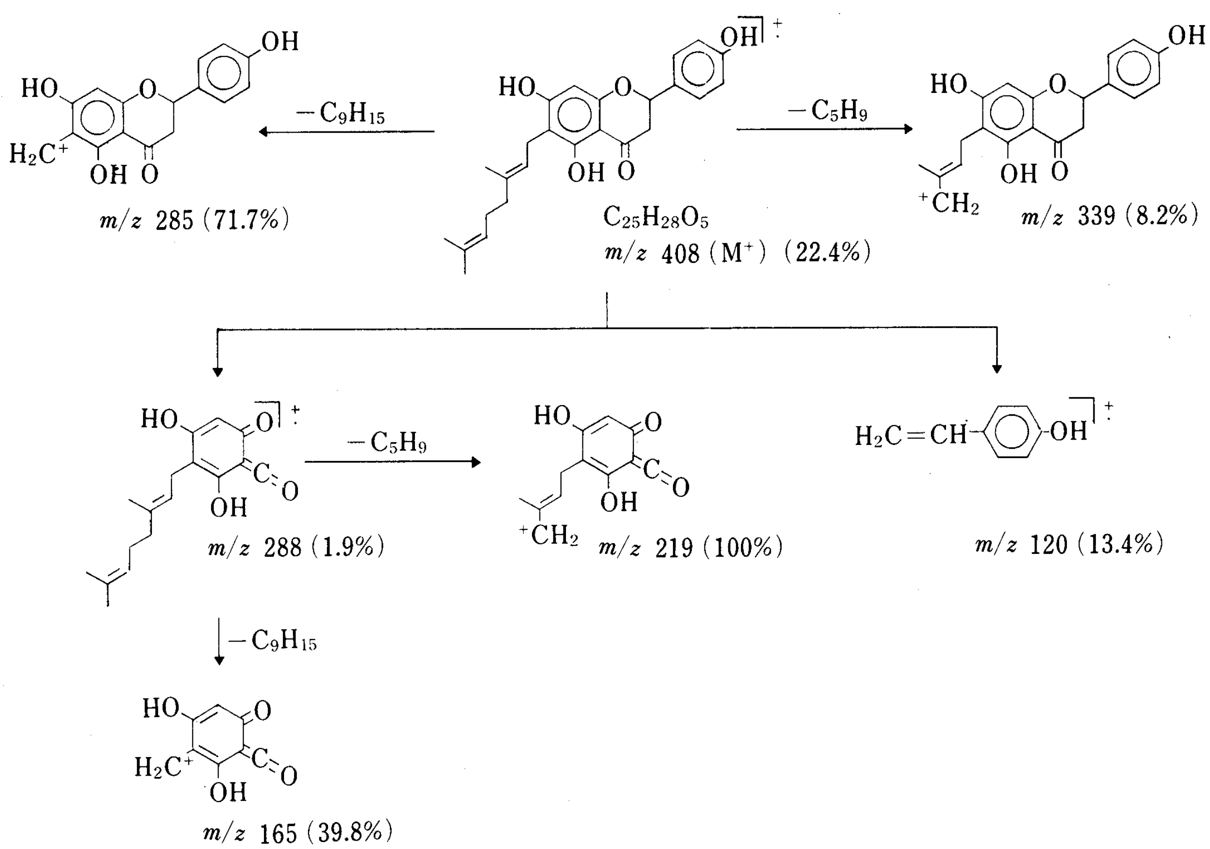
Table I. ^{13}C-NMR Data for Sophorachromone A (I), Sophoraflavanone A (II), IV and V

	I[a]	IV[a]	II[a]	II[b]	V[b]
C_2	158.1 (d)	168.1 (s)	80.3 (d)	78.2 (d)	78.3 (d)
C_3	111.9 (d)	108.6 (d)	44.1 (t)	42.0 (t)	42.0 (t)
C_4	183.4 (s)	183.4 (s)	197.9 (s)	196.6 (s)	197.1 (s)
C_5	161.3 (s)	161.0 (s)	163.2 (s)	161.2 (s)	161.6 (s)
C_6	99.9 (d)	99.2 (d)	108.9 (s)	107.0 (s)	107.1 (s)
C_7	162.8 (s)	162.0 (s)	165.4 (s)	164.4 (s)	164.7 (s)
C_8	108.2 (s)	107.1 (s)	96.9 (d)	95.3 (d)	95.4 (d)
C_{4a}	107.2 (s)	105.1 (s)	103.9 (s)	101.8 (s)	
C_{8a}	157.1 (s)	156.4 (s)	161.7 (s)	159.8 (s)	160.1 (s)
$C_{1'}$	22.6 (t)	22.2 (t)	131.6 (s)	129.3 (s)	129.5 (s)
$C_{2'}$	123.6 (d)	123.1 (d)	129.3 (d)	127.3 (d)	128.3 (d)
$C_{3'}$	136.2 (s)	131.7 (s)	116.6 (d)	115.1 (d)	115.4 (d)
$C_{4'}$	16.7 (q)	17.9 (q)	159.1 (s)	157.6 (s)	157.9 (s)
$C_{5'}$	40.9 (t)	25.8 (q)	116.6 (d)	115. 1(d)	115.4 (d)
$C_{6'}$	27.9 (t)		129.3 (d)	127.3 (d)	128.3 (d)
$C_{7'}$	125.6 (d)				
$C_{8'}$	132.1 (s)				
$C_{9'}$	18.2 (q)				
$C_{10'}$	26.2 (q)				
$C_{1''}$			22.7 (t)	21.2 (t)	
$C_{2''}$			124.2 (d)	122.5 (d)	122.9 (d)
$C_{3''}$			135.5 (s)	133.8 (s)	130.5 (s)
$C_{4''}$			16.7 (q)	15.8 (q)	17.5 (q)
$C_{5''}$			41.0 (t)	c)	25.5 (q)
$C_{6''}$			27.9 (t)	26.2 (t)	
$C_{7''}$			125.7 (d)	124.2 (d)	
$C_{8''}$			132.1 (s)	130.6 (s)	
$C_{9''}$			18.2 (q)	17.5 (q)	
$C_{10''}$			26.3 (q)	25.5 (q)	
C_2-CH_3		20.4 (q)			

Chemical shifts were measured in *a*) CD_3COCD_3 or *b*) DMSO-d_6. s, singlet; d, doublet; t, triplet; q, quartet.
c) The signal overlapped with that of the solvent.

$C_{7''}$-H)], C-2 proton [δ 5.45], C-3 protons [δ 2.6—3.3 (2H)], five aromatic protons [δ 6.03 (1H), 6.90 (2H), 7.41 (2H)], and three hydroxyl groups [δ 8.6, 9.4 (each 1H) and 12.1 (1H, chelated with C_4 carbonyl); both of which disappeared on the addition of D_2O]. The MS of II showed a major fragment at m/z 285 $[C_{16}H_{13}O_5]^+$, which indicates the loss of 123 $[C_9H_{15}]^+$ mass units from the molecular ion, suggesting the presence of a geranyl (or neryl) group (Chart 2). In view of the ^1H-NMR spectral data, the characteristic peaks at m/z 219 and 165 suggest the presence of two hydroxyl groups and a geranyl (or neryl) group on the A-ring of a flavanone. On the other hand, the fragment at m/z 120 arises from the B-ring by a retro-Diels–Alder fragmentation; this suggests the presence of only one hydroxyl group on the B-ring.

The ^{13}C-NMR spectrum of II (DMSO-d_6) showed signals at δ 78.2 and 42.0 attributable to C-2 and C-3 of flavanones. Since the signals at δ 107.0 (C-6) and 95.3 (C-8) are the same as those of sophoraflavanone B,[2b] the geranyl (or neryl) group was shown to be located at C-6 (Table 1), and this was also supported by the blue coloration in the Gibbs reaction. UV shifts after the addition of sodium acetate, aluminum chloride or sodium ethoxide showed that the three hydroxyl groups were located at C-7, C-5 and C-4′. The possibility of a geranyl group is also supported by the appearance in the ^{13}C-NMR spectrum (CD_3COCD_3) of C-4″ at δ 16.7 and C-5″ at δ 41.0, respectively.[5,6]



MS fragmentation of II

Chart 2

From these data, the structure of sophoraflavanone A (II) was concluded to be 6-geranyl-5,7,4′-trihydroxyflavanone. Since II showed a positive Cotton effect at 313 nm ($\Delta\varepsilon + 1.42$) and a negative Cotton effect at 293 nm ($\Delta\varepsilon - 6.92$) in the circular dichroism (CD) spectrum, the absolute configuration at C-2 was identified as (−)-2S-flavanone.[7)]

Experimental

Melting points were determined on a Yanagimoto MP-S3 micro melting point apparatus and are uncorrected. IR and UV spectra were taken on Nihonbunko IRA-1 and UVIDEC-1 machines, respectively. ^{1}H-NMR and ^{13}C-NMR spectra were measured with a JEOL PS-100 spectrometer at 100 MHz and 25 MHz, respectively, and chemical shifts are given in 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-01-SG-2 spectrometer with a direct inlet system. The CD and ORD spectra were recorded on a JASCO J-20A spectrometer.

Column chromatography was performed on silica gel (Wako, C-200). Thin layer chromatography (TLC) was conducted on Kieselgel G nach Stahl (Merck) and the spots were detected by spraying Gibbs reagent, ferric chloride 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 (3.5 kg) of *Sophora tomentosa* L., which were collected in Ishigaki, Okinawa prefecture in January 1982, were extracted five times with boiling MeOH. The methanolic extract (340 g) was reextracted with ether five times to afford 153 g of brown material. The ether-soluble part (60 g) was chromatographed on silica gel using *n*-hexane and *n*-hexane–acetone as solvents to give isosophoranone (180 mg), I (20 mg) and II (30 mg).

Sophorachromone A (I)——I was recrystallized from benzene-MeOH as colorless plates, mp 138—139 °C, brown under UV light, darkbrown to $FeCl_3$, blue by the addition of H_2O_2 in NaOH solution. MS *m*/*z*: 314.1495 (M^+, Calcd for $C_{19}H_{22}O_4$: 314.1516) (25%), 245.0832 ($C_{14}H_{13}O_4$: 245.0814) (83%), 219.0664 ($C_{12}H_{11}O_4$: 219.0657) (2%), 191.0314 ($C_{10}H_7O_4$: 191.0344) (100%), 165.0176 ($C_8H_5O_4$: 165.0188) (10%), 123.1165 (C_9H_{15}: 123.1175) (20%), 69.0706 (C_5H_9 : 69.0705) (47%). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): $218_{\mathrm{(sh)}}$ (4.06), 264 (3.97), 305 (2.89); $\lambda_{\max}^{\mathrm{EtOH+EtONa}}$ nm (log ε): 274 (4.20), 336 (3.54); $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ nm (log ε): 274 (3.98), 316 (2.93); $\lambda_{\max}^{\mathrm{EtOH+AcONa}}$ nm (log ε): 267 (3.84), $275_{\mathrm{(sh)}}$ (3.68). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200—3400 (OH), 1650 (C=O), 1620, 1570 (arom. C=C). ^{1}H-NMR (CD_3COCD_3) δ: 1.54, 1.59, 1.80

(each 3H, each s, $C_{3'}$, $C_{8'}$-CH_3), 2.00 (4H, br s, $C_{5'}$, $C_{6'}$-H_2), 3.43 (2H, br d, $J=7.3$ Hz, $C_{1'}$-H_2), 5.0—5.3 (2H, m, $C_{2'}$, $C_{7'}$-H), 6.22 (1H, d, $J=5.9$ Hz, C_3-H), 6.35 (1H, s, C_6-H), 8.15 (1H, d, $J=5.9$ Hz, C_2-H), 9.6 (1H, br s, C_7-OH; disappeared on the addition of D_2O), 12.7 (1H, s, C_5-OH; disappeared on the addition of D_2O). ^{13}C-NMR: (Table 1).

Sophoraflavanone A (II)——II was recrystallized from benzene–MeOH as colorless needles, mp 144—145 °C, brown under UV light, greenish-yellow to $FeCl_3$, blue to the Gibbs reaction, pink to Mg-HCl. $[\alpha]_D^{22}$ $-33°$ ($c=1.0$, EtOH). CD ($c=0.1$, EtOH) $\Delta\varepsilon^{22}$ (nm): -6.92 (293), $+1.42$ (313). MS m/z: 408.1944 (M^+, Calcd for $C_{25}H_{28}O_5$: 408.1937) (22%), 339.1238 ($C_{20}H_{19}O_5$: 339.1233) (8%), 288.1316 ($C_{17}H_{20}O_4$: 288.1362 (2%), 285.0763 ($C_{16}H_{13}O_5$: 285.0763) (72%), 219.0647 ($C_{12}H_{11}O_4$: 219.0657) (100%), 165.0188 ($C_8H_5O_4$: 165.0188 (40%), 123.1169 (C_9H_{15}: 123.1175) (8%), 120.0585 (C_8H_8O: 120.0575) (13%), 69.0697 (C_5H_9: 69.0705) (20%). UV λ_{max}^{EtOH} nm (log ε): $223_{(sh)}$ (4.10), 297 (3.60), 337 (3.13). $\lambda_{max}^{EtOH+NaOEt}$ nm (log ε): $250_{(sh)}$ (4.31), 338 (4.08). $\lambda_{max}^{EtOH+AlCl_3}$ nm (log ε): $226_{(sh)}$ (4.16), 314 (3.73). $\lambda_{max}^{EtOH+NaOAc}$ nm (log ε): 297 (3.89), 340 (3.89). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1640 (C=O), 1620, 1520 (arom. C=C). ^1H-NMR (CD_3COCD_3) δ: [1.56 (3H, s), 1.62 (6H, s), $C_{3''}$, $C_{8''}$-CH_3], 1.97 (4H, br s, $C_{5''}$, $C_{6''}$-H_2), 2.6—3.3 (2H, m, C_3-H_2), 3.24 (2H, br d, $J=7.1$ Hz, $C_{1''}$-H_2), 5.0—5.3 (2H, m, $C_{2''}$, $C_{7''}$-H), 5.45 (1H, q, $J=12.0$ Hz, 3.6 Hz, C_2-H), 6.03 (1H, s, C_8-H), 6.90 (2H, d, $J=8.8$ Hz, $C_{3'}$, $C_{5'}$-H), 7.41 (2H, d, $J=8.8$ Hz, $C_{2'}$, $C_{6'}$-H), 8.6, 9.4 (each 1H, each br s; disappeared on the addition of D_2O), 12.1 (1H, s, C_5-OH; disappeared on the addition of D_2O). ^{13}C-NMR: (Table 1).

Isosophoranone (III)——III was recrystallized from benzene–AcOEt as pale yellow needles, mp 182—183 °C. The spectral data for III were identical with those reported for isosophoranone.[2b]

Synthesis of 2-Methyl-8-prenyl-5,7-dihydroxychromone (IV)——IV was synthesized according to Bajawa[8] and recrystallized from MeOH as colorless plates, mp 187—188 °C, brown under UV light, brown to $FeCl_3$. ^1H-NMR (CD_3COCD_3) δ: 1.65, 1.82 (each 3H, each s, $C_{3'}$-CH_3), 2.42 (3H, s, C_2-CH_3), 3.41 (2H, br d, $J=7.3$ Hz, $C_{1'}$-H_2), 5.23 (1H, br t, $J=7.3$ Hz, $C_{2'}$-H), 6.07 (1H, s, C_3-H), 6.30 (1H, s, C_6-H), 9.6 (1H, br s, C_7-OH: disappeared on the addition of D_2O), 12.8 (1H, s, C_5-OH: disappeared on the addition of D_2O). ^{13}C-NMR: (Table 1).

References and Notes

1) Part XVII: Y. Shirataki, A. Manaka, I. Yokoe, and M. Komatsu, *Phytochemistry*, **21**, 2959 (1982).
2) *a)* M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.*, **26**, 1274 (1978); *b) idem, ibid.*, **26**, 3863 (1978).
3) G. D. Monache, F. D. Monache, and G. B. Marini-Bettolo, *Gazz. Chim. Ital.*, **107**, 189 (1977).
4) *a)* Y. Tomita, "Zikken Kagaku Koza (Supplementary Volume)," Vol. 5, ed. by The Chemical Society of Japan, Maruzen Co., Ltd., Tokyo, 1966, p. 928; *b) idem, ibid.*, p. 932; *c) idem, ibid.*, pp. 940—942.
5) *a)* K. Yakushijin, K. Shibayama, H. Murata, and H. Furukawa, *Heterocycles*, **14**, 397 (1980); *b)* T. Nomura and T. Fukai, *Planta Med.*, **42**, 79 (1981).
6) M. Kozawa, N. Morita, K. Baba, and K. Hata, *Yakugaku Zasshi*, **98**, 210 (1978).
7) B. A. Bohm, Flavanones and dihydroflavonols in "The Flavonoids," ed. by J. B. Harborne, T. J. Mabry, and H. Mabry, Chapman and Hall, London, 1975, p. 594; W. Gaffield, *Tetrahedron*, **26**, 3033 (1970).
8) B. S. Bajawa, Pyare Lal Khanna, and T. R. Seshadri, *Indian J. Chem.*, **9**, 1322 (1971).