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 sophoraisoflavananone A (I), mp 178—180°, C_{21}H_{24}O_{11}, and sophoraisoflavananone B (II), mp 193—195°, C_{38}H_{32}O_{16}, together with sophoronal (IV), isos Sophoronal (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_{23}H_{24}O_{12}, was also isolated. The structures of them were determined by chemical and spectroscopic studies.

Sophoraisoflavananone A (I) exhibited antifungal activity.

**Keywords**—*Sophora tomentosa* L.; Leguminoses; sophoraisoflavananone A; sophoraisoflavananone B; 1-octadecanoyl caffeate; sophoronal; isos Sophoronal; isobavachin; prenylflavanoid; antifungal activity

In the previous study,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 sophoraisoflavananone A (I), sophoraisoflavananone B (II), and a group of new phenolic compounds (III), together with sophoronal (IV), isos Sophoronal (V) and isobavachin (VI) have been isolated. The present paper deals with the structure elucidation and the antifungal activities of these compounds.

Sophoraisoflavananone A (I) was obtained as colorless needles, mp 178—180°, [α]_{D}^{22} = −17.3° (EtOH), M_{r} = 370.14 (Calc. for C_{21}H_{24}O_{11}: 370.14), C_{21}H_{22}O_{11}, 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} = 291, 330 nm) suggested the presence of flavanone or isoflavananone skeleton in I.2a) From the negative Mg-HCl test and the proton magnetic resonance (PMR) spectrum of I [(CD_{3})_{2}CO] showing a complex multiplet (3H) at δ 4.4—4.6, attributed to the protons of the ring C of an isoflavananone,3) I was considered as the isoflavananone derivatives, which was also supported by 13C-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 isoflavananones, 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

2) Location: *Keyakidai 1-1, Sakado, Saitama*, 350-02, Japan.
### Table I. CMR Spectra Data (δ: ppm from TMS in DMSO d₆)

<table>
<thead>
<tr>
<th>Carbon</th>
<th>I</th>
<th>II</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>Naringenin</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>70.7 (t)</td>
<td>78.3</td>
<td>75.5 (d)</td>
<td>70.8 (t)</td>
<td>78.8</td>
<td>78.8 (d)</td>
</tr>
<tr>
<td>3</td>
<td>44.6 (d)</td>
<td>42.0</td>
<td>73.4 (d)</td>
<td>44.7 (d)</td>
<td>43.0</td>
<td>42.4 (t)</td>
</tr>
<tr>
<td>4</td>
<td>198.0 (s)</td>
<td>197.1</td>
<td>195.2 (s)</td>
<td>198.1 (s)</td>
<td>191.0</td>
<td>196.4 (s)</td>
</tr>
<tr>
<td>4a</td>
<td>102.4 (s)</td>
<td>—</td>
<td>100.5 (s)</td>
<td>102.3 (s)</td>
<td>115.1</td>
<td>102.1 (s)</td>
</tr>
<tr>
<td>5</td>
<td>164.2 (s)</td>
<td>161.6</td>
<td>165.0 (s)</td>
<td>161.1 (s)</td>
<td>125.4</td>
<td>163.7 (s)</td>
</tr>
<tr>
<td>6</td>
<td>96.1 (d)</td>
<td>107.1</td>
<td>96.3 (d)</td>
<td>108.0 (s)</td>
<td>113.6</td>
<td>96.3 (d)</td>
</tr>
<tr>
<td>7</td>
<td>167.0 (s)</td>
<td>164.7</td>
<td>166.9 (s)</td>
<td>164.6 (s)</td>
<td>162.1</td>
<td>166.9 (s)</td>
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<tr>
<td>8</td>
<td>95.0 (d)</td>
<td>95.4</td>
<td>95.1 (d)</td>
<td>94.5 (d)</td>
<td>109.8</td>
<td>95.4 (d)</td>
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<tr>
<td>8a</td>
<td>165.5 (s)</td>
<td>160.1</td>
<td>162.8 (s)</td>
<td>161.4 (s)</td>
<td>160.9</td>
<td>163.1 (s)</td>
</tr>
<tr>
<td>1'</td>
<td>121.3 (s)</td>
<td>129.5</td>
<td>123.9 (s)</td>
<td>121.4 (s)</td>
<td>129.8</td>
<td>129.1 (s)</td>
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<tr>
<td>2'</td>
<td>156.3 (s)</td>
<td>128.3</td>
<td>154.2 (s)</td>
<td>156.4 (s)</td>
<td>128.2</td>
<td>128.5 (d)</td>
</tr>
<tr>
<td>3'</td>
<td>118.9 (s)</td>
<td>115.4</td>
<td>113.8 (s)</td>
<td>119.1 (s)</td>
<td>115.3</td>
<td>115.6 (d)</td>
</tr>
<tr>
<td>4'</td>
<td>157.9 (s)</td>
<td>157.9</td>
<td>153.4 (s)</td>
<td>157.9 (s)</td>
<td>157.7</td>
<td>157.9 (s)</td>
</tr>
<tr>
<td>5'</td>
<td>111.4 (d)</td>
<td>115.4</td>
<td>111.2 (d)</td>
<td>111.4 (d)</td>
<td>115.3</td>
<td>115.6 (d)</td>
</tr>
<tr>
<td>6'</td>
<td>127.3 (d)</td>
<td>128.3</td>
<td>128.1 (d)</td>
<td>127.3 (d)</td>
<td>128.2</td>
<td>128.5 (d)</td>
</tr>
</tbody>
</table>

|       | 17.7 (q) | 17.5 | 17.7 (q) × 2 | 17.6 | 20.7 (t) | 21.7 |
|       | 23.0 (t) | —     | 20.7 (t) | 21.7 | 23.2 (t) | 25.5 |
|       | 25.5 (q) | 25.5 | 25.5 (q) × 2 | 22.4 | 122.9 (d) | 130.8 |
|       | 123.5 (d) | 122.9 | 122.9 (d) | 130.5 | 123.6 (d) | 130.5 (s) × 2 |

|       | 26.6 (q) | 27.7 (q) |
|       | 74.3 (s) | 117.4 (d) |
|       | 130.6 (d) | 62.1 (q) | 61.8 (q) |

*a*) Signals may be interchanged.

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**Chart 1.** Fragmentation in MS of Sophoraisoflavanone A (I)
at δ 5.98 (2H), 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 D₂O).

On methylation with diazomethane, I gave tetramethyl ether (Ia), mp 135—137°, C₁₄H₂₅O₅, 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-d₆) 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 CH₃ and C₄H₇ 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 sophoraisoaffavanone A (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 C₂₇H₄₆O₄ which gave the PMR spectrum (CDCl₃) 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). 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 C₁₅H₂₀O₅: 280.1310), C₁₅H₂₀O₅ 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, 500.0x842.0), a pair of doublets at δ 5.91 (1H, d, J = 2 Hz) and 6.08 (1H, d, J = 2 Hz) in trimethylallyl ether of I.

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 trimethylallyl ether of I.

6) The physical data (UV, PMR and MS) of Ib were almost the same to that of dihydrosophorinol.42)
\[ J = 7 \text{ Hz} \], 2.84 (2H, br. t, \( J = 7 \text{ Hz} \)) and two ortho aromatic protons [\( \delta 6.67 (1H, d, J = 8.7 \text{ Hz}) \],
7.12 (1H, d, \( J = 8.7 \text{ Hz} \))].

It contains an alcoholic function together with the acidic one (PMR, IR), and the losses of COOH and CH₂OH are observed in MS. The minor product (Id): mp 115–116°, \( \text{C}_{25}\text{H}_{36}\text{O}_4 \), also comes from B-ring. The spectrum data of this compound were in good agreement with those of 5-methoxy-2,2-dimethylchromene-6-carboxylic acid derived from sophoranol.\(^7\) The structure of 1c can be assigned to the hydroxy-acid of the same aromatic skeleton of Id. Accordingly, the structure of 1c was established to be 3-hydroxy-2-(5-methoxy-2,2-dimethyl-6-chromanyl) propanoic acid.

In conclusion, the structure of sophoraisoflavnone 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 isoflavonones.\(^8\) Further work on the stereochemistry of these compounds is in progress.

Sopheraflavone B (II) was obtained as colorless needles, mp 193–195°, \([\alpha]_D^25 = -25°\) (EtOH), \( M^+ = 340.1306 \) (Calcd. for \( \text{C}_{20}\text{H}_{29}\text{O}_5 \): 340.1309), \( \text{C}_{26}\text{H}_{30}\text{O}_5 \), 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 \( \gamma\gamma\)-dimethylallyl group [\( \delta 1.61 (6H, s) \], 3.22 (2H, br. d, \( J = 7.9 \text{ Hz} \)), 5.20 (1H, br. t, \( J = 7.9 \text{ Hz} \))], C-2 proton [\( \delta 5.45 (1H, q, J = 12.1 \text{ Hz} \), 3.5 Hz)], C-3 protons [\( \delta 2.60-3.13 (2H, m) \)], five aromatic protons [\( \delta 6.03 (1H, s) \], 6.92 (2H, d, \( J = 8.8 \text{ Hz} \)), 7.42 (2H, d, \( J = 8.8 \text{ Hz} \))], and three hydroxyl groups, one of them was chelated hydroxyl proton at \( \delta 12.15 \) (disappeared by the addition of D₂O). In the MS of II, the retro-Diels-Alder cleavage of the molecular ion (M⁺ = 340) led to major fragments at \( m/e 220 \) [(\( \text{C}_{12}\text{H}_{12}\text{O}_4 \)], A-ring] and \( m/e 120 \) [(\( \text{C}_9\text{H}_4\text{O}^- \)], 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 \( \gamma\gamma\)-dimethylallyl group in A-ring at C-6 or C-8.

Wenkert et al.\(^11\) have reported the 13C chemical shifts of C-6 and C-8 were appeared at \( \delta 96.3 \) and 95.4 in the CMR spectrum of naringenin, respectively. CMR spectrum of II showed at \( \delta 107.1 \) (C-6) and 95.4 (C-8). Consequently, \( \gamma\gamma\)-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 sophoraisoflavnone B was represented by II.\(^12\)

Since the specific optical rotation of II had a minus (−) sign, as other natural flavonones,\(^30\) II most probably has an (S)-configuration at C-2.

III was obtained as colorless needles, mp 108–110°, \( M^+ = 432.3217 \) (Calcd. for \( \text{C}_{27}\text{H}_{44}\text{O}_4 \): 432.3237), \( \text{C}_{27}\text{H}_{44}\text{O}_4 \), exhibited positive ferric chloride reaction and ortho-diphenol reaction. The IR spectrum suggested the presence of hydroxyl, \( \alpha\beta\)-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

8) Only two optical active isoflavonone derivatives, sophorol\(^9\) from \( S. \textit{japonica} \) and isosporonol\(^40\) from \( S. \textit{tomentosa} \), have been isolated so far.
12) Recently, Ashish Nagar et al. have reported the synthesis of 6-C-prenyl naringenin (\textit{Tetrahedron Lett.}, \textbf{1978}, 2031).
at $\delta$ 0.85 (3H, t, $J=4.5$ Hz), polymethylene group at $\delta$ 1.23 (ca. 32H, s), -COOCH$_2$CH$_2$ at $\delta$ 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 $\delta$ 6.7–7.1 (3H, m) showed the presence of ABX type protons on aromatic ring, a pair of doublets ($J=16$ Hz) at $\delta$ 6.24 (1H) and 7.46 was assigned the H$_a$ and H$_b$ of Ar-CH$_3$=CH$_2$-COOR, trans, respectively.

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

Whereas, III was hydrolysed with alkali to give caffeic acid and an aliphatic alcohol, C$_n$H$_{2n+1}$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).

![Gas chromatogram of III](image)

**Fig. 2.** GC-MS of III

![Molecular structures](image)

**Fig. 3**
Consequently, III was formulated as Fig. 3. M. Komatsu, one of the authors, has already reported trans-cafeic acid docosyl ester. \( \text{C}_{22}\text{H}_{42}\text{O}_7 \) from \( \text{S. subprostrata} \), and III was an additional one of this series. Furthermore, sophoronal (IV), isosophoronane (V), and isobavacin (VI) were also isolated.

The antifungal activities of I, VII, VIIa, VIIb, and \( \text{l-maackiain} \) were shown in Table II.

### Table II. Antifungal Activities of I, VII, VIIa, VIIb and \( \text{l-Maackiain} \)

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>VII</th>
<th>VIIa</th>
<th>VIIb</th>
<th>( \text{l-Maackiain} )</th>
<th>Erythromycin</th>
<th>Cetyltrimethyl chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Staphylococcus aureus} ) 209 P</td>
<td>18.5</td>
<td>10</td>
<td>±</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>29</td>
</tr>
<tr>
<td>( \text{Escherichia coli} )</td>
<td>9.5</td>
<td>8.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>( \text{Bacillus subtilis} )</td>
<td>21</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>( \text{PCI 219} )</td>
<td>±</td>
<td>±</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>( \text{Aspergillus niger NHL 5088} )</td>
<td>±</td>
<td>±</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>( \text{Aspergillus fumigatus IAM 2400} )</td>
<td>13</td>
<td>11</td>
<td>0</td>
<td>±</td>
<td>±</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>( \text{Penicillium citrinum IAM 7003} )</td>
<td>9.5</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>( \text{Candida albicans Yu 1290} )</td>
<td>±</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>±</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

Inhibitory circle (diameter, mm) by Disk methods.

IIa: diacetate of compound VII, VIIa: 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-I 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 \( \delta \) (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 x 3 mm) packed with 1% OV-1. Column chromatography was carried out with Wakoel 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. \( \text{H}_2\text{SO}_4 \) 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 \( \text{Sophora tomentosa} \) 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-\( \text{AcOEt} \) (with increasing concentrations of \( \text{AcOEt} \) 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, \( \text{l-maackiain} \), medicagol, stigmasterol were isolated. 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.

**Sophoralsoffavanone A** (I)—I was recrystallized from benzene as colorless needles, mp 178—180°, \( [\alpha]_D^2 -17.3^\circ (c=0.26, \text{EtOH}) \), brown under UV light, greenish brown to \( \text{FeCl}_3 \) dark blue to Gibbs reaction. TLC Rf: 0.67 (benzene-\( \text{AcOEt}=1:1 \)) (solv. 1). Anal. Calcd. for \( \text{C}_{22}\text{H}_{44}\text{O}_7 \): C, 68.09; H, 5.99. Found:

C, 68.56; H, 6.17. MS m/z: 370.1435 (M+, Calcd. for C₈H₁₆O₇: 370.1415), 218.1288 (C₆H₄O₂: 218.1305) base peak, 203.1064 (C₅H₈O₄: 203.1071), 163.0763 (C₄H₇O₃: 163.0758), 153.0186 (C₃H₂O: 153.0186). UV ƛ_max (nm) (log e): 291 (4.43), 330 (4.02). ƛ_max (nm) (log e): 302 (4.23), 331 (4.49). IR ν_max cm⁻¹: 3400 (OH), 1640 (C=O), 1610, 1600 (arom. C=O), 1390 (CH₃). PMR [(CD₃)₂CO]: 1.68, 1.78 (each 3H, each s, =CH₂), 3.39 (2H, br. d, J = 6.4 Hz, Ar-CH₂-CH₂=), 3.75 (3H, s, -OCH₃), 4.4–4.6 (3H, m, C₆-H₃, C₇-H₃), 5.30 (1H, br. t, J = 6.4 Hz, C₄-H₃), 5.98 (2H, s, C₆-H₂), 6.84 (1H, d, J = 8.4 Hz, C₃-H₂), 8.68 (1H, d, J = 8.4 Hz, C₇-H), 8.6, 9.6 (each 1H, br. OH x 2; disappeared by the addition of D₂O). 12.4 (1H, s, C₂-OH; disappeared by the addition of D₂O).

Methylation of 1(a) —To a solution of 1 in MeOH, an ether solution of CH₃I was added at 0°C. After standing at room temp. for 24 hr, the solvent was removed and residue was recrystallized from MeOH as colorless prisms, mp 135–137°C, no color to FeCl₃. MS m/z: 412.1896 (M⁺, Calcd. for C₈H₁₆O₇: 412.1884), 232.1455 (C₄H₈O₄: 232.1461) base peak, 217.1208 (C₅H₈O₄: 217.1227), 181.0498 (C₃H₆O₃: 181.0494). UV ƛ_max (nm) (log e): 284, 320 (sh). IR ν_max cm⁻¹: 2920, 1388 (CH₃), 1765 (C=O), 1605, 1575 (arom. C=O). PMR [(CD₃)₂CO]: 1.66, 1.77 (each 3H, each s, =CH₂), 3.35 (2H, br. d, J = 6.7 Hz, Ar-CH₂-CH₂=), 3.72 (3H, s, -OCH₃), 3.81 (6H, s, -OCH₃ x 2), 3.88 (3H, s, -OCH₃), 4.15 (1H, q, J = 9.2 Hz, 6.1 Hz, C₆-H₂), 4.45–4.55 (2H, m, C₆-H₂), 5.21 (1H, br. t, J = 6.7 Hz, C₅-H₂), 6.15 (1H, d, J = 2.1 Hz, C₇-H), 6.22 (1H, d, J = 2.1 Hz, C₂-H), 6.70 (1H, d, J = 8.7 Hz, C₅-H), 6.97 (1H, d, J = 8.7 Hz, C₇-H).

Acid-catalyzed Cyclization of 1 (Formation of Ib) —A mixture of 1 (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/z: 370.1407 (M⁺, Calcd. for C₈H₁₆O₇: 370.1415), 218.1301 (C₅H₈O₄: 218.1305) base peak, 203.1057 (C₅H₈O₄: 203.1073), 163.0733 (C₄H₇O₃: 163.0758), 162.0654 (C₃H₆O₃: 162.0679), 153.0182 (C₃H₆O₃: 153.0187). UV ƛ_max (nm) (log e): 292, 332 (sh). IR ν_max cm⁻¹: 303, 385. UV ƛ_max (nm) (log e): 330. IR ν_max cm⁻¹: 3300 (OH), 1640 (C=O), 1600, 1480 (arom. C=O). PMR (CDCl₃): 1.38 (6H, s, -OCH₃(C₆H₅)), 1.82 (2H, br. t, J = 6.7 Hz, C₅-H₂), 2.84 (2H, br. t, J = 6.2 Hz, Ar-CH₂-CH₂=), 3.84 (3H, s, -OCH₃), 4.2–4.5 (3H, m, C₆-H₂, C₅-H₂), 5.85–6.20 (2H, m, C₆-H₂), 6.69 (1H, d, J = 8.7 Hz, C₇-H), 6.97 (1H, d, J = 8.7 Hz, C₅-H), 12.11 (1H, s, C₂-OH; disappeared by the addition of D₂O).

Hydrogen Peroxide Cleavage of Ib (Formation of Ic and Id) —30% H₂O₂ (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°C, then at 50°C and aged with dil. HCl. The reaction mixture was extracted with AcOEt. The AcOEt extract was purified on a silica gel column (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/z: 280.1239 (M⁺, Calcd. for C₁₃H₁₄O₇: 280.1310) (48.8%), 249.1192 (C₁₂H₁₀O₇: 249.1125) (100%), 225 (M⁺-COOH) (16.2%), 225.0772 (C₁₂H₁₀O₆: 225.0762) (6.4%), 218.1208 (C₁₀H₈O₅: 218.1305) (21.2%), 205.1205 (C₁₀H₇O₄: 205.1227) (16.4%), 195.0497 (C₈H₇O₄: 195.0499) (25.1%), 179.0654 (C₈H₆O₃: 179.0707) (21.0%), 163 (C₈H₆O₂-OH: 163.0758) (18.5%), 149.0455 (C₆H₄O₂: 149.0449) (25.0%). [The data were given by the nominal MS].

UV ƛ_max (nm) (log e): 279. IR ν_max cm⁻¹: 3600, 3525, 1700, 1605, 1580, 1480, 1295, 1070. PMR (CDCl₃): 1.36 (6H, s, -OCH₃(C₆H₅)), 1.81 (2H, br. t, J = 7 Hz, -CH₂-CH₂=), 2.84 (2H, br. t, J = 7 Hz, Ar-CH₂-CH₂=), 3.87 (3H, s, -OCH₃), 3.9–4.4 (3H, m, -CH₂-CH₂=), 6.67 (1H, d, J = 8.7 Hz, -CH=), 7.00 (2H, br. s, -COOH + OH; disappeared by the addition of D₂O), 7.12 (1H, d, J = 8.7 Hz, -CH=).
(6H, s, ≈CH₃), 2.60—3.13 (2H, m, C₆H₅), 3.22 (2H, br. d, J = 7.9 Hz, Ar—CH₂—CH₂H), 5.20 (1H, br. t, J = 7.9 Hz, C₆H₅—CH₂—CḦ₂C̈₂), 5.45 (1H, q, J = 12.1 Hz, 3.5 Hz, C₆H₅—H), 6.03 (1H, s, C₆H₅—H), 6.92 (2H, d, J = 8.8 Hz, C₆H₅—H), 7.42 (2H, d, J = 8.8 Hz, C₆H₅—H), 8.5—11.0 (2H, br, OH × 2; disappeared by the addition of D₂O), 12.15 (1H, s, C₆H₅—OH; disappeared by the addition of D₂O).

**Compound III**—Recrystallization from MeOH gave colorless needles, mp 108—110°, dark blue under UV light, FeCl₃ (+), SrCl₂—NH₄ (+). TLC RF: 0.62 (Solvent 1). MS m/e: 432.3217 (M⁺, Calcd. for C₃₇H₄₂O₄: 432.3237), 180.0421 (C₆H₅O₂; 180.0421) base peak, 163.0396 (C₆H₅O₂; 163.0395). UV λ_max nm (log ε): 248 (4.11), 301 (sh) (4.03), 332 (4.13). IR ν max cm⁻¹: 3480, 3300 (OH), 2920, 2840, 1480, 1460 (CH), 1690, 1290, 1180 (conj. ester), 1610, 1540 (arom. C=O).

**Hydrolysis of III**—III was saponified with 5% KOH/90% MeOH for 3 hr at 60—70° with stirring under N₂ gas flow. The reaction mixture was partitioned between ether and H₂O. 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 (C₆H₅OH) with IR spectrum, but this was proved to be a mixture of C₆H₅OH [MS m/e: 224=M—H₂O], C₆H₅OH [MS m/e: 238=M—H₂O], C₆H₅OH [MS m/e: 252=M—H₂O], C₆H₅OH [MS m/e: 286=M—H₂O], and C₆H₅OH [MS m/e: 298=M—H₂O] as a fractional part of 1.8: 0.7: 91.8: 0.5: 5.2% by GC—MS. The H₂O layer was neutralized with dil. HCl and extracted with EtOAc. After the evaporation of solvent the residue was recrystallized from MeOH—H₂O to give pale yellow powder, caffeic acid which was identified by direct comparison (TLC, UV, mp and IR) with an authentic sample.

**Sophorol (IV)**—Recrystallization from a mixture of benzene—petroleum ether gave colorless powder, mp 101—103°, [α]D 20 +215° (c = 1.0, pyridine), brown under UV light, greenish brown to FeCl₃, purple blue to Gibbs reaction. TLC RF: 0.67 (Solvent 1). MS m/e: 384.1239 (M⁺, Calcd. for C₃₇H₄₂O₄: 384.1207). This was identified by the direct comparison (mixed mp, TLC, UV, IR, PMR and MS) with an authentic sample.

**Isosiphorolone (V)**—Recrystallization from a mixture of benzene—AcOEt gave pale yellow needles, mp 182—183°, [α]D 20 0° (c = 0.13, EtOH), brown under UV light, greenish brown to FeCl₃, purple blue to Gibbs reaction. TLC RF: 0.68 (Solvent 1). MS m/e: 438.2018 (M⁺, Calcd. for C₃₇H₄₄O₄: 438.2040), 383.1480 (C₂₉H₃₂O₄; 383.1492), 221.0801 (C₁₄H₂₀O₄; 221.0812), 220.0737 (C₁₄H₁₉O₄; 220.0735), 218.1300 (C₁₄H₁₉O₄; 218.1305). The spectral data (UV, IR and PMR) of V were very similar to that of isosiphorolone but this was isolated as a racemate like other natural isoavananones.

**Isoavamin (VI)**—Recrystallization from a mixture of MeOH—H₂O gave colorless needles, mp 200—202°, [α]D 20 —46° (c = 0.13, EtOH), negative to FeCl₃ and Gibbs reaction. TLC RF: 0.49 (Solvent 1). MS m/e: 324.1363 (M⁺, Calcd. for C₃₇H₄₂O₄: 324.1360) base peak, 269.0812 (C₂₉H₃₂O₄; 269.0813), 240.0791 (C₂₉H₃₂O₄; 240.0786), 149.0264 (C₆H₅O₂; 149.0238), 120.0567 (C₆H₅O₂; 120.0574). UV λ_max nm: 288 (sh), 348. IR ν max cm⁻¹: 3240 (OH), 1640 (C=O), 1600, 1520 (arom. C=O), 1390 (CH₃). PMR ((CD₃)₂SO): 1.62 (6H, s, ≈CH₃), 2.6—3.1 (2H, m, C₆H₅—H), 3.22 (2H, br. d, J = 7.4 Hz, Ar—CH₂—CH₂H), 5.20 (1H, br. t, J = 7.4 Hz, C₆H₅—CH₂—CH₂C₂), 5.45 (1H, q, J = 12.1 Hz, 3.5 Hz, C₆H₅—H), 6.03 (1H, s, C₆H₅—H), 6.92 (2H, d, J = 8.8 Hz, C₆H₅—H), 7.42 (2H, d, J = 8.8 Hz, C₆H₅—H), 8.5—11.0 (2H, br, OH × 2; disappeared by the addition of D₂O).

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