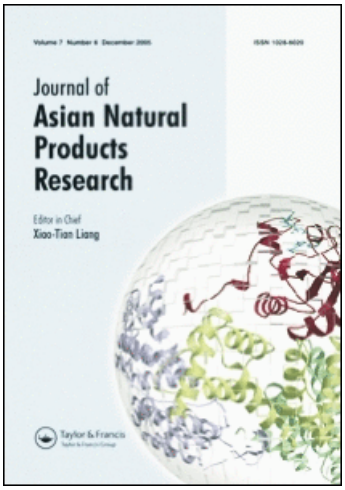

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Three new isoprenylated flavonoids from the roots of *Sophora flavescens*

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Three new isoprenylated flavonoids from the roots of *Sophora flavescens*

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Three new flavonoids isoprenylated as 2,2-dimethyl-dihydropyran groups, named sophoranodichromanes A–C (**1**–**3**), have been isolated from the roots of *Sophora flavescens*, together with the known compounds, chrysophanol (**4**), soyasapogenol B (**5**) and β-sitosterol (**6**). Their structures have been elucidated by spectroscopic methods.

Keywords: *Sophora flavescens*; Leguminosae; Isoprenylated flavonoids; Sophoranodichromanes A–C

1. Introduction

The dried root of *Sophora flavescens* Aiton (Leguminosae) (Radix Sophorae Flavescentis; Chinese name "Kushen") is a well-known traditional Chinese medicine for the treatment of acute dysentery, gastrointestinal hemorrhage, eczema and colpitis [1,2]. It contains several quinolizidine alkaloids, prenylated flavonoids and oleanene glycosides [3–9]. During our studies on the constituents of the *Sophora* plants, the ether-soluble fraction from the ethanolic extract of the roots of *S. flavescens* was separated by repeated column chromatography over silica gel to afford three new flavonoids isoprenylated as 2,2-dimethyl-dihydropyran groups, named sophoranodichromanes A–C (**1**–**3**), together with the known compounds, chrysophanol (**4**) [10,11], soyasapogenol B (**5**) [12,13] (figure 1) and β-sitosterol (**6**) [14]. Chrysophanol was isolated from this genus and soyasapogenol B was isolated from this plant for the first time. This paper is concerned with the isolation and structure elucidation of the new compounds (**1**–**3**).

2. Results and discussion

Sophoranodichromane A (**1**) ($C_{25}H_{28}O_6$ by HR-ESIMS) was obtained as pale yellow needles from light petroleum, mp 272–273°C, $[\alpha]_D^{22}$ −27.0 (*c* 0.52, $CHCl_3$). It gave a positive

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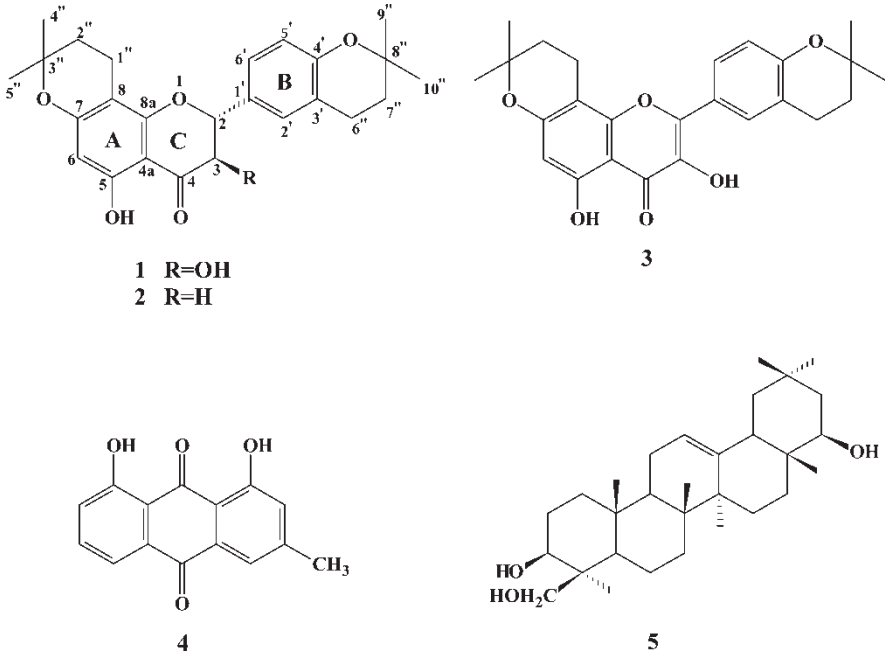

Figure 1. Structures of compounds **1**–**5**.

reaction with $FeCl_3$, showing its phenolic nature. Its IR spectrum shows absorption bands characteristic of hydroxyl group (3515 cm^{-1}), conjugated carbonyl group (1645 cm^{-1}), and aromatic ring functionalities (1586 and 1489 cm^{-1}). The UV spectrum is consistent with that of a flavanonol with maxima at 340 (sh) and 297 nm. The ^{1}H NMR spectrum of **1** shows two 2,2-dimethyl-dihydropyran groups each in rings A and B with signals at δ 2.83 (2H, t, $J = 6.7$ Hz), 2.52 (2H, m), 1.85 (2H, t, $J = 6.7$ Hz), 1.78 (2H, m), 1.33 (9H, s), and 1.31 (3H, s), which is further supported by fragment ions at *m/z* 221 (63) ($[A_1 + H]^+$) and 204 (17) ($B_1^{+\cdot}$) in the EIMS due to RDA cleavage of a flavanonol. The ^{1}H NMR spectrum also exhibits signals due to two hydroxyl groups [δ 11.39 (1H, s, chelated) and 4.64 (1H, br s)], which disappear with D_2O exchange, an aromatic proton singlet (δ 5.87, s), ABX type aromatic protons [δ 7.28 (1H, dd, $J = 8.1$, 3.0 Hz), 7.25 (1H, d, $J = 3.0$ Hz) and 6.85 (1H, d, $J = 8.1$ Hz) (in $CDCl_3$)], and two coupled protons of H-2 and H-3 in a flavanonol skeleton [δ 5.06 (1H, d, $J = 11.6$ Hz) and 4.59 (1H, d, $J = 11.6$ Hz) (in acetone-d_6 + D_2O)]. The ^{13}C NMR spectrum of **1** contains signals of four oxygenated aromatic carbons (δ 164.5, 162.4, 161.3, 155.9), one carbonyl carbon (δ 198.8), and the signals due to C-2 (δ 84.8) and C-3 (δ 73.4) of a flavanonol. The location of the 2,2-dimethyl-dihydropyran group in A ring was established at C-7 and C-8 by the HMBC experiment, in which the protons at δ 1.78 (H_2-2″) correlate with C-8 (δ 102.2), the protons at δ 2.52 (H_2-1″) couple with C-8 (δ 102.2), C-8a (δ 161.3), and C-7 (δ 164.5), and the chelated hydroxyl group at δ 11.39 (OH-5) correlates with C-6 (δ 98.2) bearing an isolated proton at δ 5.87, C-5 (δ 162.4), and C-4a (δ 101.9). The position of the same group in B ring at C-3′ and C-4′ was also deduced by the correlations of the protons at δ 1.85 (H_2-7″) with C-3′ (δ 121.9), the protons at δ 2.83 (H_2-6″) with C-3′ (δ 121.9), C-4′ (δ 155.9), and C-2′ (δ 130.6) bearing a proton at δ 7.32 which subsequently correlates with C-2 (δ 84.8), C-4′ (δ 155.9) and C-6′ (δ 128.2) (figure 2). With the aid of HMBC and HMQC experiments, all proton and carbon signals were fully assigned.

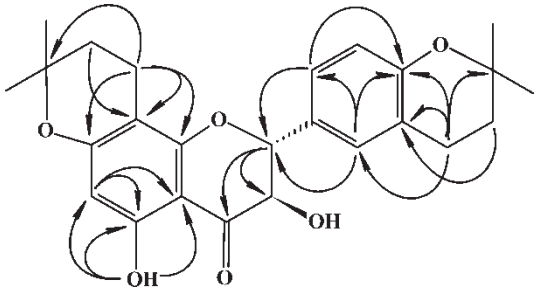

Figure 2. Selected HMBC correlations of **1**.

The absolute configuration at C-2 was determined as *R* by CD analysis, which shows a positive Cotton effect at 324 nm and a negative one at 297 nm [6,15]. Subsequently, the absolute configuration at C-3 was determined as *R* from the value of the coupling constant between H-2 and H-3 ($J = 11.6$ Hz). Thus, **1** was characterized as (2*R*,3*R*)-7,8,bis-3′,4′-(2,2-dimethyl-chromano)-5-hydroxyflavanonol.

Sophoranodichromane B (**2**) ($C_{25}H_{28}O_5$ by HR-ESIMS) was obtained as white fine needles from light petroleum, mp 278–279°C, $[\alpha]_D^{22}$ −55.9 (*c* 0.23, $CHCl_3$). It gave a positive reaction with $FeCl_3$. Its IR and UV spectra are similar to those of **1**. Comparison of the ^{1}H NMR spectral data of **2** with those of **1** reveals that the chemical shifts and splitting patterns of **2** agree well with those of **1** except that the signals at δ 5.09 (1H, d, $J = 11.4$ Hz, H-2) and 4.64 (2H, m, H-3, OH-3) in **1** have been replaced by three reciprocally coupled protons at δ 5.47 (1H, dd, $J = 13.0$, 3.0 Hz), 3.16 (1H, dd, $J = 17.0$, 13.0 Hz), and 2.78 (1H, dd, $J = 17.0$, 3.0 Hz) being assigned to H-2, H-3a and H-3b in a flavanone skeleton (table 1). ^{13}C NMR data of **2** are also identical to those of **1** except for the noticeable up-field shift of C-3 ($\Delta\delta$ −30.4 ppm) in **2** (table 2). Therefore, **2** was deduced to be the 3-desoxy derivative of **1**. This is also supported by the fragment ions at *m*/*z* 221 (8) ($[A_1 + H]^+$) and 188 (70) ($B_1^{+\cdot}$) in the EIMS of **2** due to RDA cleavage, of which the latter is 16 mass units less than that of **1** [*m*/*z* 204 (17)]. The absolute configuration at C-2 was *S* as determined from the CD analysis, which shows a positive Cotton at 321 nm and a negative one at 293 nm [6,15]. Thus, **2** was deduced to be (2*S*)-7,8,bis-3′,4′-(2,2-dimethyl-chromano)-5-hydroxyflavanone.

Sophoranodichromane C (**3**) ($C_{25}H_{26}O_6$ by HR-ESIMS) was obtained as yellow powder, mp 267–268°C. It gave a positive reaction with $FeCl_3$. Its IR spectrum shows absorptions characteristic of hydroxyl (3278 cm^{-1}), conjugated carbonyl (1656 cm^{-1}), and aromatic ring (1555, and 1495 cm^{-1}). The UV spectrum exhibits maximum absorptions at 371, 273, 255, and 230 (sh) nm, indicating a flavonol skeleton. Two additional oxygenated olefinic carbons (δ 147.1, and 137.4), instead of the signals due to H-2 and H-3 in ^{1}H NMR spectrum, and the up-fielded carbonyl carbon (δ 177.0) in ^{13}C NMR spectrum also reveal the presence of a flavonol skeleton. In addition, the following signals appear in the ^{1}H NMR spectrum of **3**: a chelated aromatic hydroxyl group [δ 11.87 (1H, s)], an olefinic hydroxyl group [δ 7.97 (1H, s)], a singlet aromatic proton [δ 6.11 (1H, s)], ABX aromatic protons [δ 8.05 (1H, br s), 8.01 (1H, br d, $J = 8.7$ Hz), 6.88 (1H, d, $J = 8.7$ Hz)], and the protons in two units of 2,2-dimethyl-dihydropyran group [δ 2.93 (2H, t, $J = 6.6$ Hz), 1.93 (2H, t, $J = 6.6$ Hz), 1.38 (6H, s) and 2.89 (2H, t, $J = 6.6$ Hz), 1.88 (2H, t, $J = 6.6$ Hz), 1.36 (6H, s)]. The two 2,2-dimethyl-dihydropyran groups in the flavonol skeleton were also determined unambiguously to be at C-7, C-8 and C-3′, C-4′ by HMBC cross peaks at δ 2.93 (H_2-1″)

Table 1. ^{1}H NMR spectral data (δ, ppm) for compounds **1**–**3** (J in Hz).

Proton	***1*** [a]	***1*** [b]	***1*** [c]	***2*** [d]	***2*** [b]	***3*** [a]
2	5.09 (1H, d, 11.4)	4.98 (1H, d, 12.0)	5.06 (1H, d, 11.6)	5.47 (1H, dd, 13.0, 3.0)	5.32 (1H, dd, 13.2, 3.0)	
3	4.64 (1H, m)	4.53 (1H, dd, 12.0, 1.8)	4.59 (1H, d, 11.6)	3.16 (1H, dd, 17.0, 13.0)	3.05 (1H, dd, 17.0, 13.2)	
				2.78 (1H, dd, 17.0, 3.0)	2.76 (1H, dd, 17.0, 3.0)	
3-OH	4.64 (1H, br s)	3.53 (1H, d, 1.8)				7.97 (1H, s)
5-OH	11.39 (1H, s)	10.95 (1H, s)		11.88 (1H, s)	11.78 (1H, s)	11.87 (1H, s)
6	5.87 (1H, s)	6.00 (1H, s)	5.83 (1H, s)	5.82 (1H, s)	5.96 (1H, s)	6.11 (1H, s)
2′	7.32 (1H, m)	7.25 (1H, d, 3.0)	7.27 (1H, m)	7.28 (1H, m)	7.20 (1H, d, 2.2)	8.05 (1H, br s)
5′	6.77 (1H, d, 9.0)	6.85 (1H, d, 8.1)	6.73 (1H, d, 9.0)	6.77 (1H, d, 9.0)	6.82 (1H, d, 8.2)	6.88 (1H, d, 8.7)
6′	7.32 (1H, m)	7.28 (1H, dd, 8.1, 3.0)	7.27 (1H, m)	7.28 (1H, m)	7.17 (1H, dd, 8.2, 2.2)	8.01 (1H, br d, 8.7)
1″	2.52 (2H, m)	2.55 (2H, m)	2.45 (2H, m)	2.59 (2H, m)	2.58 (2H, m)	2.93 (2H, t, 6.6)
2″	1.78 (2H, m)	1.74 (2H, m)	1.74 (2H, m)	1.79 (2H, m)	1.75 (2H, m)	1.93 (2H, t, 6.6)
4″,5″	1.33 (3H, s) 1.31 (3H, s)	1.35 (3H, s) 1.32 (3H, s)	1.28 (3H, s) 1.26 (3H, s)	1.33 (3H, s) 1.31 (3H, s)	1.34 (3H, s) 1.32 (3H, s)	1.38 (6H, s)
6″	2.83 (2H, t, 6.7)	2.83 (2H, t, 6.7)	2.78 (2H, t, 6.7)	2.83 (2H, t, 6.8)	2.81 (2H, t, 6.9)	2.89 (2H, t, 6.6)
7″	1.85 (2H, t, 6.7)	1.83 (2H, t, 6.7)	1.79 (2H, t, 6.7)	1.84 (2H, t, 6.8)	1.83 (2H, t, 6.9)	1.88 (2H, t, 6.6)
9″,10″	1.33 (6H, s)	1.36 (6H, s)	1.28 (6H, s)	1.32 (6H, s)	1.35 (6H, s)	1.36 (6H, s)

[a] Measured in acetone-d_6 (500 MHz).
[b] In $CDCl_3$ (300 MHz).
[c] In acetone-d_6 + D_2O (500 MHz).
[d] In acetone-d_6 (400 MHz).

Table 2. ^{13}C NMR spectral data (δ, ppm) for compounds **1**–**3**.

Carbon	***1***[a]	***1***[b]	***2***[a]	***2***[b]	***3***[a]
2	84.8 (d)	83.3 (d)	79.5 (d)	79.0 (d)	147.1 (s)
3	73.4 (d)	72.2 (d)	43.0 (t)	43.2 (t)	137.4 (s)
4	198.8 (s)	195.9 (s)	197.0 (s)	196.0 (s)	177.0 (s)
4a	101.9 (s)	100.2 (s)	101.1 (s)	100.8 (s)	104.8 (s)
5	162.4 (s)	160.9 (s)	162.0 (s)	161.5 (s)	160.0 (s)
6	98.2 (d)	97.8 (d)	97.1 (d)	97.4 (d)	100.2 (d)
7	164.5 (s)	164.0 (s)	163.2 (s)	163.0 (s)	161.4 (s)
8	102.2 (s)	101.4 (s)	102.9 (s)	102.7 (s)	101.2 (s)
8a	161.3 (s)	160.1 (s)	160.7 (s)	160.0 (s)	155.1 (s)
1′	129.7 (s)	127.4 (s)	128.3 (s)	127.4 (s)	124.1 (s)
2′	130.6 (d)	128.9 (d)	130.6 (d)	129.7 (d)	130.6 (d)
3′	121.9 (s)	121.0 (s)	121.5 (s)	121.1 (s)	122.5 (s)
4′	155.9 (s)	154.9 (s)	154.9 (s)	154.5 (s)	157.3 (s)
5′	118.1 (d)	117.5 (d)	117.6 (d)	117.6 (d)	118.6 (d)
6′	128.2 (d)	126.6 (d)	126.1 (d)	125.4 (d)	128.2 (d)
1″	17.2 (t)	16.1 (t)	16.5 (t)	16.3 (t)	17.1 (t)
2″	32.7 (t)	31.8 (t)	32.0 (t)	32.0 (t)	32.6 (t)
3″	77.4 (s)	76.4 (s)	76.4 (s)	76.1 (s)	77.3 (s)
4″,5″	27.6 (q)[c]	27.2 (q)[c]	26.8 (q)[c]	27.1 (q)[c]	27.2 (q)
	26.9 (q)[c]	26.3 (q)[c]	26.1 (q)[c]	26.4 (q)[c]	27.2 (q)
6″	23.5 (t)	22.6 (t)	22.7 (t)	22.6 (t)	23.6 (t)
7″	33.7 (t)	32.7 (t)	32.9 (t)	32.7 (t)	33.6 (t)
8″	75.4 (s)	74.6 (s)	74.6 (s)	74.5 (s)	76.3 (s)
9″,10″	27.54 (q)[c]	27.0 (q)[c]	26.70 (q)[c]	26.93 (q)[c]	27.5 (q)
	27.50 (q)[c]	27.0 (q)[c]	26.67 (q)[c]	26.89 (q)[c]	27.5 (q)

[a] Measured in acetone-d_6 (125 MHz).
[b] In $CDCl_3$ (75 MHz).
[c] Assignments could be interchangable within the same column.

with C-8 (δ 101.2), C-8a (δ 155.1), and C-7 (δ 161.4); δ 1.93 (H_2-2″) with C-8 (δ 101.2); δ 2.89 (H_2-6″) with C-3′ (δ 122.5), C-2′ (δ 130.6), and C-4′ (δ 157.3); and δ 1.88 (H_2-7″) with C-3′ (δ 122.5). Thus, **3** was identified as 7,8,bis-3′,4′-(2,2-dimethyl-chromano)-5-hydroxyflavonol.

Compounds **4**–**6** were identified as chrysophanol, soyasapogenol B and β-sitosterol respectively by comparing their spectral data (mp, $[\alpha]_D$, UV, ^{1}H and ^{13}C NMR, EIMS) with the reported ones [10–14].

3. Experimental

3.1 General experimental procedures

Melting points were determined on an XT-4 micro-melting point apparatus and were uncorrected. Optical rotations were measured on a Jasco P-1020 digital polarimeter. UV spectra were recorded on a Shimadzu UV-260 UV–visible recording spectrophotometer. CD spectra were recorded on a Jasco J-715 spectropolarimeter. IR spectra were taken on an AVATAR 360 FT-IR spectrophotometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were run on Bruker DRX-400, 500 and Varian Gemini 2000 300 instruments with TMS as internal standard. EIMS were recorded on an HP 5989A mass spectrometer. ESIMS were obtained on a PE Mariner mass spectrometer and HR–ESIMS were recorded on an AB QSTAR Pulsar mass spectrometer. Silica gel H (200–300 mesh, Qingdao Haiyang, China) was used for column chromatography and precoated silica gel plates GF_{254} (10–40 μm, Yantai, China)

were used for analytical TLC. Spots on the plate were observed under UV light and visualized by spraying with 10% H_2SO_4 followed by heating.

3.2 Plant material

Plant material was purchased from Huayu Materia Medica Co., Ltd., Shanghai, in February 2001, and identified as the roots of *Sophora flavescens* Aiton (Leguminosae) by Dr. Dao-feng Chen. A voucher specimen (KS-SH-0102) has been deposited in the Herbarium of Materia Medica, Department of Pharmacognosy, School of Pharmacy, Fudan University, Shanghai.

3.3 Extraction and isolation

Pulverized roots of *S. flavescens* (14 kg) were extracted with aqueous 1% H_2SO_4 (4 ×) to give the total alkaloids (250 g), and were then air-dried and extracted with 95% EtOH (15.0 L, 6 × each time) at room temperature. The EtOH extract (1440 g) was suspended in water (2.5 L) and partitioned with Et_2O (3.0 L, 6 ×). The Et_2O-soluble fraction (195 g) was then subjected to silica-gel column chromatography eluting with light petroleum (60–90°C), light petroleum–EtOAc (50:1, 20:1, 15:1, 10:1, 5:1, 3:1, 1:1) and EtOAc to give nine fractions based on TLC profiles. Fraction 2-A (8.51 g) was subjected to silica-gel chromatography using light petroleum–EtOAc (100:1, 20:1) as solvent system to give **4** (4 mg), and fraction 2-B was purified by recrystallization with light petroleum to afford **2** (88 mg). Fraction 3-A (3.24 g) was chromatographed on silica gel eluting with light petroleum–Me_2CO (20:1) to give **3** (5 mg), fractions 3-B and 3-C were also purified by recrystallization with light petroleum to yield **6** (626 mg) and **1** (56 mg) respectively. Fraction 6 (2.92 g) was eluted with $CHCl_3$–MeOH (100:1, 20:1) on silica gel to afford **5** (32 mg).

Sophoranodichromane A (**1**): obtained as pale yellow needles from light petroleum (60–90°C); 56 mg; mp 272–273°C; $[\alpha]_D^{22}$ −27.0 (*c* 0.52, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) 340 sh (3.56), 297 (4.31), 218 (4.49), 206 (4.52); CD (MeOH) $[\theta]_{324}$ +7270, $[\theta]_{297}$ −38800, $[\theta]_{268}$ +5790, $[\theta]_{226}$ +22190; IR (KBr) ν_{max} (cm^{-1}) 3515, 3054, 2975, 2842, 1645, 1586, 1489, 1352, 1259, 1156, 1117, 1000; ^1H NMR data, see table 1; ^{13}C NMR data, see table 2; EIMS *m/z* 424 $[M]^+$ (10), 395 (8), 222 (8), 221 (63), 204 (17), 203 (14), 202 (100), 177 (9), 175 (15), 165 (50), 149 (11), 148 (14); ESIMS *m/z* 425.2 $[M + H]^+$, 447.3 $[M + Na]^+$; HR-ESIMS *m/z* 425.1984 ($[M + H]^+$, calcd. for $C_{25}H_{29}O_6$, 425.1964).

Sophoranodichromane B (**2**): obtained as white fine needles from light petroleum (60–90°C); 88 mg; mp 278–279°C; $[\alpha]_D^{22}$ −55.9 (*c* 0.23, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) 340 sh (3.44), 294 (4.20), 217 (4.38), 206 (4.42); CD (MeOH) $[\theta]_{321}$ + 12230, $[\theta]_{293}$ −60750, $[\theta]_{256}$ +7910, $[\theta]_{223}$ +29090; IR (KBr) ν_{max} (cm^{-1}) 3437, 2974, 2930, 2847, 1643, 1587, 1497, 1481, 1260, 1231, 1155, 1117, 1083; ^1H NMR data, see table 1; ^{13}C NMR data, see table 2; EIMS *m/z* 409 $[M + 1]^+$ (14), 408 $[M]^+$ (50), 221 (8), 192 (15), 189 (15), 188 (70), 176 (17), 175 (100), 165 (38), 133 (30); ESIMS *m/z* 409.2 $[M + H]^+$, 431.2 $[M + Na]^+$; HR-ESIMS *m/z* 431.1838 ($[M + Na]^+$, calcd. for $C_{25}H_{28}O_5Na$, 431.1834).

Sophoranodichromane C (**3**): obtained as yellow powder, 5 mg; mp 267–268°C; UV (MeOH) λ_{max} (nm) (log ε) 371 (4.25), 273 (4.25), 255 (4.21), 230 sh (4.17), 206 (4.47); IR (KBr) ν_{max} (cm^{-1}) 3278, 2968, 2925, 2850, 1656, 1605, 1555, 1495, 1451, 1367, 1326, 1268, 1231, 1159, 1120, 1077; ^1H NMR data, see table 1; ^{13}C NMR data, see table 2; EIMS *m/z* 422 $[M]^+$ (100), 407 (5), 405 (7), 367 (70), 312 (10), 311 (29), 189 (10), 176 (10), 165 (26), 69

(27), 55 (42), 43 (42), 41 (43); HR-ESIMS *m/z* 445.1632 ($[M + Na]^+$, calcd. for $C_{25}H_{26}O_6Na$, 445.1627).

Chrysophanol (**4**): obtained as orange prisms from light petroleum (60–90°C); 4 mg; mp 185–187°C; $C_{15}H_{10}O_4$; UV (MeOH) λ_{max} (nm) (log ε) 429 (3.91), 287 (3.90), 276 (3.89), 255 (4.20), 224 (4.42); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)12.14 (1H, s, OH-8), 12.04 (1H, s, OH-1), 7.83 (1H, d, $J = 7.4$ Hz, H-5), 7.68 (1H, t, $J = 8.1$ Hz, H-6), 7.67 (1H, s, H-4), 7.30 (1H, d, $J = 8.6$ Hz, H-7), 7.11 (1H, s, H-2), 2.47 (3H, s, Ar-Me); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 192.7 (C-9), 182.1 (C-10), 162.9 (C-8), 162.6 (C-1), 149.5 (C-3), 137.1 (C-6), 133.8 (C-5a), 133.4 (C-4a), 124.7 (C-2), 124.5 (C-7), 121.5 (C-4), 120.0 (C-5), 116.0 (C-8a), 113.9 (C-1a), 22.4 (Ar-Me); EIMS *m/z* 255 $[M + 1]^+$ (17), 254 $[M]^+$ (100), 239 $[M - Me]^+$ (4), 237 $[M - OH]^+$ (5), 226 $[M - CO]^+$ (13), 225 (6), 198 $[M - 2CO]^+$ (8), 197 (10), 152 (9), 115 (5).

Soyasapogenol B (**5**): obtained as white needles from light petroleum (60–90°C); 32 mg; mp 260–262°C; $[\alpha]_D^{28}$ +86.3 (*c* 0.1, MeOH); $C_{30}H_{50}O_3$; UV (MeOH) λ_{max} (nm) (log ε) no absorption above 210; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 5.25 (1H, br s, H-12), 4.22 (1H, m), 3.44 (3H, m), 1.25, 1.11, 1.04, 0.94, 0.91, 0.89, 0.87 (each 3H, s, Me-23, 25, 26, 27, 28, 29, 30); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 144.1 (C-13), 122.4 (C-12), 81.0 (C-3), 76.7 (C-22), 64.6 (C-24), 56.1 (C-5), 47.9 (C-9), 46.4 (C-19), 45.0 (C-18), 43.0 (C-14), 42.2 (C-4), 41.7 (C-21), 39.9 (C-8), 38.6 (C-1), 37.5 (C-10), 36.8 (C-17), 33.3 (C-7), 32.8 (C-29), 30.6 (C-20), 28.4 (C-28), 28.3 (C-15), 27.8 (C-16), 26.0 (C-2), 25.4 (C-27), 23.9 (C-11), 22.5 (C-23), 20.0 (C-30), 18.6 (C-6), 17.0 (C-26), 16.2 (C-25); EIMS *m/z* 458 $[M]^+$ (2), 440 (1), 426 (1), 412 (1), 409 (1), 407 (1), 234 (100), 224 (9), 219 (43), 216 (10), 203 (6), 201 (10), 187 (9), 176 (28), 175 (27), 161 (11), 145 (8), 133 (11), 57 (32), 56 (30), 43 (32), 41 (28).

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