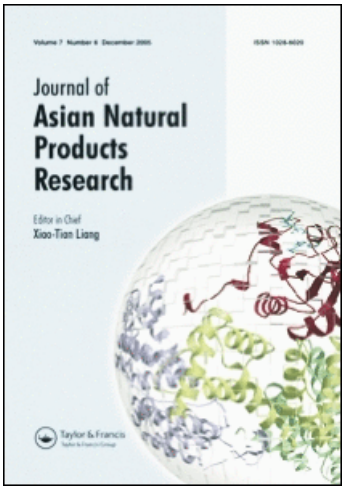

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A NEW COUMARONOCHROMONE FROM *SOPHORA JAPONICA*

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A new coumaronochromone derivative, sophorophenolone (**1**), along with 13 known compounds, *l*-maackiain (**2**), medicagol (**3**), 7-*O*-methylpseudobaptigenin (**4**), pseudobaptigenin (**5**), 7,3′-di-*O*-methylorobol (**6**), genistein (**7**), prunetin (**8**), daidzein (**9**), formononetin (**10**), Di-*O*-methyldaidzein (**11**), quercetin (**12**), kaempferol (**13**) and isorhamnetin (**14**) were isolated from pericarps of *Sophora japonica* L. The structure of compound 1 was established by UV, IR, MS, and one-dimensional and two-dimensional NMR spectroscopy, including DEPT, NOESY, $^{1}H-^{1}H$ COSY, HMQC, and HMBC experiments.

Keywords: *Sophora japonica*; Leguminosae; Sophorophenolone

INTRODUCTION

The fruits of *Sophora japonica* L. (Leguminosae) were commonly used as hemostatics in traditional Chinese medicine, and flavonoids were discovered as hemostatic constituents from the buds *S. japonica* [1]. To our knowledge, no phytochemical studies on the pericarp parts have been reported. We have taken the pericarps of this plant for systematic phytochemical investigations, and obtained 14 compounds including sophorophenolone (**1**), *l*-maackiain (**2**), medicagol (**3**) (Fig. 1), 7-*O*-methylpseudobaptigenin (**4**), pseudobaptigenin (**5**), 7,3′-di-*O*-methylorobol (**6**), genistein (**7**), prunetin (**8**), daidzein (**9**), formononetin (**10**), Di-*O*-methyldaidzein (**11**), quercetin (**12**), kaempferol (**13**) and isorhamnetin (**14**). Compound **1** is a new coumaronochromone. Compounds **2**–**6**, **8**–**11** and **14** were isolated from this plant for the first time. Here, we report the isolation and structural elucidation of **1**.

RESULTS AND DISCUSSION

Ethanol (95%) extracts of pericarps of *S. japonica* were suspended in H_2O and then extracted with petroleum ether, ethyl acetate and *n*-BuOH, successively. The ethyl acetate soluble part was subjected to usual chromatographic methods to afford compound **1**.

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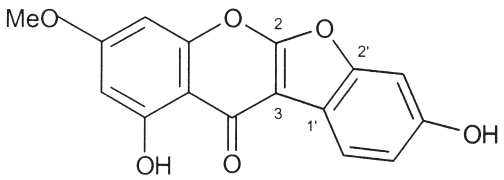

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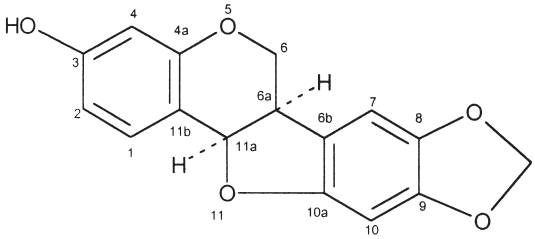

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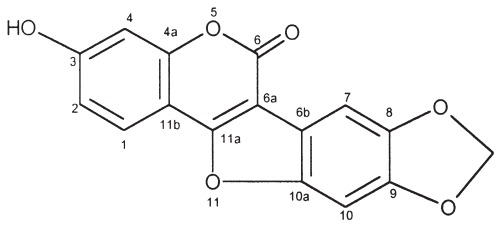

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FIGURE 1 The chemical structures of compounds **1**–**3**

Compound **1** was obtained as colorless fine needles (MeOH), m.p. $> 300°C$, it was formulated as $C_{16}H_{10}O_6$ on the basis of elemental analysis and the mass spectrum (M^+ at *m/z* 298) and gave positive Mg–HCl test. Its IR spectrum revealed the presence of hydroxy (3247 cm^{-1}), conjugated carbonyl (1651 cm^{-1}), and aromatic (1599, 1584, 1520 and 1507 cm^{-1}) groups. The ultraviolet absorption bands at λ_{max}^{MeOH} 256, 283, 330 nm indicated similar characteristic absorption bands of isoflavone [2,3]. The addition of $AlCl_3$ or $AlCl_3$–HCl caused bathochromic shift in the UV spectrum. The evidence suggests the presence of chelated phenolic hydroxyl group. The ^1H NMR spectrum (Table I) of **1** exhibited two aromatic signals as a pair of *meta*-coupled doublets (δ 6.47, 1H, d, $J = 2.3$ Hz and δ 6.83, 1H, d, $J = 2.3$ Hz), which were assigned to the A-ring protons (H-6 and H-8) of a 5,7-dioxygenated isoflavone, and three aromatic signals as ABX system (δ 6.93, 1H, dd, $J = 8.4$ and 2.0 Hz; δ 7.11, 1H, d, $J = 2.0$ Hz and δ 7.71, 1H, d, $J = 8.4$ Hz) attributable, as in cajanin [4], to the B-ring protons of an isoflavone with 2′,4′-dioxygenation [5]. A methoxyl singlet, observed at δ 3.86 in the ^1H NMR spectrum of **1**, was correlated with a quaternary carbon at δ 164.66 in the HMBC spectrum. The latter signal showed correlations to both H-6 and H-8 in the HMBC spectrum. Hence the ^{13}C NMR signal at δ 164.66 was assigned to C-7 with methoxy group substitution. The latter was also supported by the methoxyl signal showing NOE correlations to both H-6 and H-8 in the NOESY experiment.

TABLE I The NMR spectral data of compound **1** (DMSO-d_6)

No.	^{13}C	^{1}H	*H M B C*
2	164.71		
3	97.55		7.71(6′)
4	178.24		
5	162.02		6.47(6), 12.91(5-OH)
6	98.84	6.47(d, 2.3)	6.83(8), 12.91(5-OH)
7	164.66		3.86(7-OMe), 6.47(6), 6.83(8), 12.91(5-OH)
8	93.95	6.83(d, 2.3)	6.47(6)
9	154.61		6.83(8)
10	103.97		6.47(6), 6.83(8), 12.91(5-OH)
1′	113.30		6.93(5′), 7.11(3′)
2′	150.16		7.11(3′), 7.71(6′)
3′	98.98	7.11(d, 2.0)	6.93(5′)
4′	156.51		6.93(5′), 7.11(3′), 7.71(6′)
5′	114.02	6.93(dd, 8.4, 2.0)	7.11(3′)
6′	121.29	7.71(d, 8.4)	
5-OH		12.91(s)	
7-OMe	56.27	3.86(s)	
4′-OH		9.98(s)	

However, the ^{1}H NMR spectrum of **1** lacked a characteristic isoflavone 2-H singlet (cf. **4**–**11**) and therefore must possess a modified isoflavone-type skeleton. A notable feature of the ^{1}H NMR spectrum of **1** is that all the aromatic proton signals appear at significantly lower field when compared with those of the corresponding 2′-hydroxyisoflavones [5]. This effect is at least partly due to deshielding of the C-4 carbonyl group [6]. When the UV, MS, ^{1}H NMR and ^{13}C NMR data are taken into account, compound **1** can be most logically deduced as a 5,4′-dihydroxy-7-methoxyisoflavone in which the C-2 and 2′ positions are linked by an ether oxygen to form a tetracyclic (coumaronochromone) ring system as in lupinalbins [7] and oblonginol [8]. The fact that compound **1** slowly affords a blue–brown color with Gibbs reagent/ammonia vapor is a further proof that the 2′-OH group is substituted and that only the H-bonded 5-OH with a free para position is involved in the reaction [5]. Finally, two hydroxy signals (δ 12.91 and δ 9.98) were assigned to locate at C-5 and C-4′ according to literature [7,8]. The proposed structure 5,4′-dihydroxy-7-methoxycoumaronochromone, was also supported by ^{13}C NMR data and two dimensional NMR experiments (Table I). Compound **1** was a new coumaronochromone derivative, named as sophorophenolone.

Compounds **2**–**6**, **10** and **11** were identified by comparing their physical and spectral data with the literature values: *l*-maackiain (**2**) [9,10], medicagol (**3**) [9,11,12], 7-*O*-methylpseudobaptigenin (**4**) [13], pseudobaptigenin (**5**) [14], 7,3′-di-*O*-methylorobol (**6**) [15,16], formononetin (**10**) [17], Di-*O*-methyldaidzein (**11**) [18]. Compounds **7**–**9** and **12**–**14** were identified by comparison of the spectra data with those for authentic samples: genistein (**7**), prunetin (**8**), daidzein (**9**) quercetin (**12**), kaempferol (**13**) and isorhamnetin (**14**).

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined by an Ellectrothermal 9200 micro melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer model 241 polarimeter. UV and IR spectra were measured on a Shimadzu UV-1601 and on a Perkin–Elmer 983, respectively. All NMR spectra were run on a Bruker DRX-400 instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C, using standard pulse sequences.

Chemical shifts are reported on the δ scale in parts per million downfield from TMS. Carbon multiplicities were determined in DEPT-135 and DEPT-90 experiments. All two dimensional NMR spectra were recorded using pulsed field gradients. One-bond $^{1}H-^{13}C$ correlations were observed in a HMQC experiment. Long-range $^{1}H-^{13}C$ correlations were observed in HMBC experiments. EI–MS spectra were obtained on a Finnigan FTMS-2000 mass spectrometer. Column chromatography was performed on Si gel (Marine Chemical Factory in Qingdao), and Sephadex LH-20 (Pharmacia).

Plant Material

Fruits of *S. japonica* L. were collected from mature trees, growing in Nanjing, China, in November 1998, and identified by Prof. Luoshan Xu, China Pharmaceutical University. A voucher specimen (No. CPUT-981120) has been deposited in the herbarium of China Pharmaceutical University.

Extraction and Isolation

Dried and powdered pericarps of *S. japonica* (7.8 kg) were extracted three times with 95% EtOH using ultrasonic apparatus for 3 h. After the solvents were removed under reduced pressure, the residue dissolved in hot water. This residue was left in the refrigerator overnight and filtered. The filtrate was partitioned against petroleum ether, EtOAc and *n*-BuOH, successively. The EtOAc-soluble fraction was concentrated and subjected to Si gel column chromatography, eluting with petroleum ether–EtOAc (50:1) followed by stepwise addition of EtOAc to yield 12 fractions. Fraction 5 (13.2 g) was subjected to Si gel (petroleum ether–EtOAc, 50:3) and Sephadex LH-20 (MeOH) chromatography to give compounds **4** (15 mg), and **11** (10 mg). Fraction 6 (15.6 g) was subjected to Si gel (petroleum ether–EtOAc, 10:1), and Sephadex LH-20 (MeOH) chromatography to give compound **2** (40 mg), **3** (20 mg), **5** (60 mg) and **10** (48 mg). Fraction 7 (15.7 g) was subjected to Si gel (petroleum ether–EtOAc, 10:2), and Sephadex LH-20 (MeOH) chromatography to give compounds **8** (30 mg), and **9** (25 mg). Fraction 8 (26.9 g) was subjected to silica gel (petroleum ether–EtOAc, 9:3), and Sephadex LH-20 (MeOH) chromatography to give compounds **1** (25 mg), **6** (5 mg), and **7** (10 g). Fraction 9 (16.1 g) was subjected to silica gel (petroleum ether–EtOAc, 10:4), and Sephadex LH-20 (MeOH) chromatography to give compounds **12** (45 mg), **13** (80 mg), and **14** (10 mg).

Sophorophenolone (**1**) Colorless fine needles (MeOH), m.p. $>$ 300°C; UV (MeOH) λ_{max} nm (log ε): 256 (4.53), 283 (4.24), 330 (3.65); +NaOAc: 256, 282, 330; + $AlCl_3$: 236sh, 268, 284sh, 302sh, 322sh, 375; +NaOAc/HCl: 236sh, 268, 284sh, 302sh, 322sh, 375. IR ν_{max}^{KBr} cm^{-1}: 3247, 1651, 1599, 1584, 1520, 1507, 1475, 1462, 1444, 1384, 1331, 1309, 1234, 1211, 1193, 1168, 1114, 1129, 1097, 1044, 1017, 949, 844, 833, 816. EI–MS (*m/z*): 298 $[M]^+$. Elemental analysis (%): found: C 62.40, H 3.40; calcd. For $C_{16}H_{10}O_6$: C 64.43, H 3.38. ^{1}H (DMSO-d_6) and ^{13}C NMR (DMSO-d_6) spectral data see Table I.

l-Maackiain (**2**) Colorless fine needles (MeOH), mp 242°C; $[\alpha]_D^{25} = -255°$ (acetone, *c* 1.0); UV (MeOH) λ_{max} nm: 280sh, 286, 308. IR ν_{max}^{KBr} cm^{-1}: 3430, 1628, 1596, 1505, 1033, 925. EI–MS (*m/z*): 284 $[M]^+$. ^{1}H NMR ($CDCl_3$): 7.36 (1H, d, $J = 8.4$, H-1), 6.55 (1H, dd, $J = 8.4$ and 2.5 Hz, H-2), 6.41 (1H, d, $J = 2.5$ Hz, H-4), 3.64 (1H, t, $J = 10.9$ Hz, H-6_{ax}), 4.22 (1H, dd, $J = 10.9$ and 4.9 Hz, H-6_{eq}), 3.47 (1H, m, H-6a), 6.72 (1H, s, H-7), 6.43 (1H, s, H-10), 5.47 (1H, d, $J = 6.9$ Hz, H-11a), 5.89 and 5.92 (2H, each d, $J = 1.3$ Hz, $-OCH_2O-$). ^{13}C NMR ($CDCl_3$): 132.14 (C-1), 109.77 (C-2), 157.03 (C-3), 103.70 (C-4), 156.69 (C-4a), 66.48 (C-6), 40.23 (C-6a), 117.93 (C-6b), 104.72 (C-7), 141.76 (C-8), 148.15 (C-9), 93.84 (C-10), 154.27 (C-10a), 78.47 (C-11a), 112.75 (C-11b), 101.29 ($-OCH_2O-$).

Medicagol (**3**): Colorless fine needles (MeOH), m.p. $> 300°C$; UV (MeOH) λ_{max} nm: 218, 265, 303, 345. IR ν_{max}^{KBr} cm^{-1}: 3300, 1710, 1630, 1600, 1580, 1040, 940. EI–MS (*m/z*): 296 $[M]^+$. ^1H NMR (DMSO-d_6): 7.85 (1H, d, $J = 8.4$ Hz, H-1), 6.94 (1H, dd, $J = 8.4$ and 2.1 Hz, H-2), 6.91 (1H, d, $J = 2.1$ Hz, H-4), 7.58 (1H, s, H-7), 7.30 (1H, s, H-10), 6.16 (2H, s, $-OCH_2O-$), 10.72 (1H, s, 3-OH). ^{13}C NMR (DMSO-d_6): 122.97 (C-1), 103.40 (C-2), 157.64 (C-3), 99.06 (C-4), 154.82 (C-4a), 161.54 (C-6), 104.48 (C-6a), 131.80 (C-6b), 114.18 (C-7), 146.18 (C-8), 147.32 (C-9), 95.04 (C-10), 150.18 (C-10a), 160.12 (C-11a), 118.15 (C-11b), 102.40 ($-OCH_2O-$).

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