Phenolic Compounds Isolated from the Roots of *Sophora stenophylla*

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A new prenylated flavanone glucoside (sophoraflavanone I 7-*O*-β-glucopyranoside) and three new resveratrol oligomers, stenophyllols A—C, were isolated from the roots of *Sophora* (*S.*) *stenophylla* along with six known flavonoids and three known resveratrol oligomers. Their structures were determined by spectroscopic analysis of correlation spectroscopy involving long-range coupling and nuclear Overhouser effect experiments.

Key words *Sophora stenophylla*; Leguminosae; prenylated flavanone; resveratrol oligomer; sophoraflavanone I 7-*O*-β-glucopyranoside; stenophyllol A

In the course of studies on the chemical constituents in the genus *Sophora*, we have described the presence of oligostilbenes derived from a resveratrol (3,5,4′-trihydroxystilbene) in some *Sophora* species.[1] The occurrence of oligostilbenoids phytochemically characterizes the species belonging to *Pseudosophora* and *Sophora*, with exception of two series (Flavescentes and Rubriflorae).[2] Here our attention was drawn to the chemical constituents of *S. stenophylla* A. GRAY (series Sericiae, section *Sophora*, subgenus *Sophora*) which is a herbaceous plant and native to the U.S.A. to reinforce the phytochemical evidence. On the other hand, we have sometimes encountered stereochemically ambiguous structures and unreasonable assignments in NMR spectral data during our previous structural elucidation of oligostilbenoids. These discrepancies need to be settled and have accelerated our research on oligostilbenoid chemistry.

Purification with column chromatography of an acetone extract of the roots of the *S. stenophylla* resulted in isolation of 13 phenolic compounds (seven flavonoids and six oligostilbenes). In the present paper, the structural elucidation of the compounds by correlation spectroscopy involving long-range coupling (COLOC) spectra and nuclear Overhauser effect (NOE) experiments is described.

Compound **5** was obtained as a colorless amorphous powder and gave an $[M-H]^-$ ion peak at *m/z* 811 in negative ion fast atom bombardment mass spectrometry (FAB-MS) corresponding to the molecular formula $C_{45}H_{48}O_{14}$. In the ^{1}H-NMR spectrum, a set of three mutually coupled protons at δ 2.78 (dd, J=16.9, 3.2 Hz), 3.09 (dd, J=16.9, 12.8 Hz) and 5.68 (dd, J=12.8, 3.2 Hz) was assignable to H-3 and H-2 in a 2′-oxygenated flavanone skeleton.[3] The ^{1}H-NMR spectrum further showed the presence of a lavandulyl group [δ 1.45, 1.51, 1.59 (3H each, s, vinyl Me), 2.28, 2.60 (2H each, m, CH_2), 2.66 (1H, m, CH), 4.44 (2H, br s, CH_2=) and 4.99 (1H, t like m, CH=)], which was further confirmed by the ^{13}C–^{1}H shift correlation spectroscopy (COSY), three aromatic protons in singlet (δ 6.29, 6.52 and 7.24), a *p*-oxygenated phenyl [δ 6.85, 7.22 (2H each, d, J= 9.0 Hz)], a 3,5-dioxygenated phenyl [δ 6.20 (2H, d, J= 2.0 Hz) and 6.27 (1H, t, J=2.0 Hz)], two aliphatic methines on a dihydrobenzofuran ring [δ 4.37 (d, J=6.9 Hz) and 5.45 (d, J=6.9 Hz)], five phenolic hydroxyl groups [δ 8.13 (×2), 8.43, 8.90 and 12.18 (chelated)] and a sugar moiety [δ 2.82—3.88 (9H, m) and 5.09 (1H, d, J=6.9 Hz, an anomeric proton)]. The analysis of ^{1}H-, ^{13}C-NMR and the MS fragmentation patterns suggested that **5** was a β-glucopyranoside of sophoraflavanone I (**4**).[4] In the NOE experiment, the aromatic proton (δ 6.29) assignable to H-6 was enhanced when the anomeric proton was irradiated. Therefore, the structure of **5** was characterized as sophoraflavanone I 7-*O*-β-glucopyranoside, and this is the first isolation of a flavanostilbene glycoside.

Compound **11** (stenophyllol A), a yellow solid, showed an $[M-H]^-$ ion peak at *m/z* 903 in the negative ion FAB-MS corresponding to the molecular formula $C_{56}H_{40}O_{12}$, which suggested that **11** was a stilbene tetramer. The ^{1}H-NMR spectrum showed the presence of three sets of *ortho*-coupled aromatic protons assignable to three 4-hydroxyl phenyl groups [δ 7.16 (2H, d, J=8.3 Hz, H-2a, 6a), 6.81 (2H, d, J=8.3 Hz. H-3a, 5a); 6.81 (2H, d, J=8.5 Hz, H-2b, 6b), 6.55 (2H, d, J=8.5 Hz, H-3b, 5b); 7.49 (2H, d, J=8.5 Hz, H-2d, 6d), 6.89 (2H, d, J=8.5 Hz, H-3d, 5d)], four sets of *meta*-coupled aromatic protons on a 1,2,3,5-tetrasubstituted benzene ring [δ 6.60 (1H, d, J=2.0 Hz, H-12a), 6.35 (1H, br s, H-14a); 5.81 (1H, d, J=2.2 Hz, H-12b), 5.29 (1H, d, J=2.2 Hz, H-14b); 5.91 (1H, d, J=2.0 Hz, H-12c), 5.22 (1H, d, J=2.0 Hz, H-14c); 6.40 (1H, d, J=1.9 Hz, H-12d), 6.58 (1H, br s, H-14d)], four olefinic protons [δ 7.53 (1H, dd, J=9.8, 2.0 Hz, H-2c), 6.22 (1H, dd, J=9.8, 2.0 Hz, H-3c), 6.17 (1H, dd, J=9.8, 2.0 Hz, H-5c), 7.17 (1H, obscured by H-2a and 6a)], a sequence of aliphatic methine protons successively coupled in this order [δ 5.46 (1H, d, J=4.4 Hz, H-7b), 3.92 (1H, dd, J=8.3, 4.4 Hz, H-8b), 4.63 (1H, d, J=8.3 Hz, H-8c)] and two sets of mutually coupled aliphatic methine protons [δ 5.79 (1H, d, J=12.2 Hz, H-7a), 4.29 (1H, br d, J=12.2 Hz, H-8a); 5.89 (1H, d, J=12.2 Hz, H-7d), 4.58 (1H, br d, J=12.2 Hz, H-8d)] in addition to nine phenolic hydroxyl groups (δ 7.64, 7.82, 8.00, 8.38, 8.42, 8.50, 8.59, 8.71 and 8.74). In the ^{13}C-NMR spectrum, an α,β-unsaturated carbonyl group was observed at δ 187.7 (C-4c). The ^{13}C–^{1}H shift correlation spectroscopy (CH COSY) was able to supply the complete assignment of all protonated carbons (Table 1). In the ^{1}H–^{1}H long rang COSY (HH long-range COSY) spectrum, an oxymethine proton (H-7a) had a correlation with H-2a(6a) on ring

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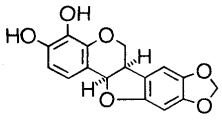

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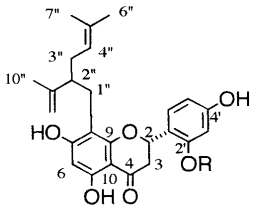

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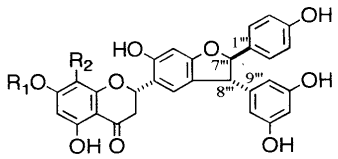
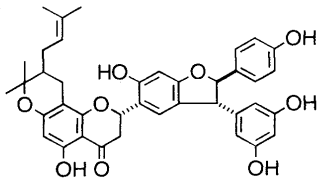
3: R = Me



4: R1 = H, R2 = lavandulyl
5: R1 = glc, R2 = lavandulyl
6: R1 = H, R2 = isoprenyl



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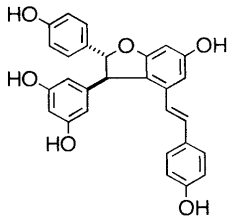

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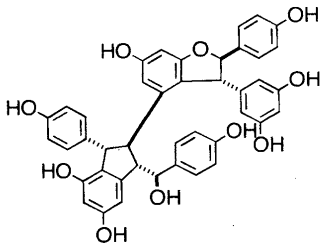

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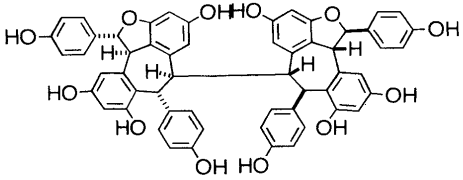

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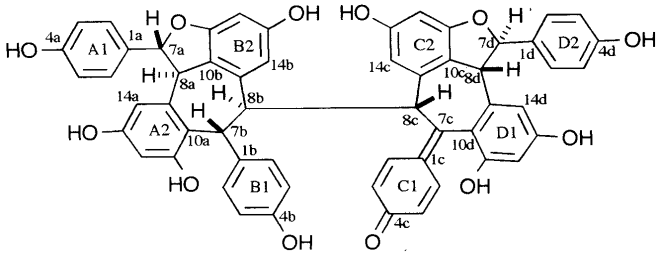

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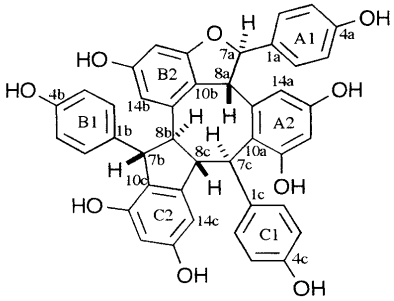

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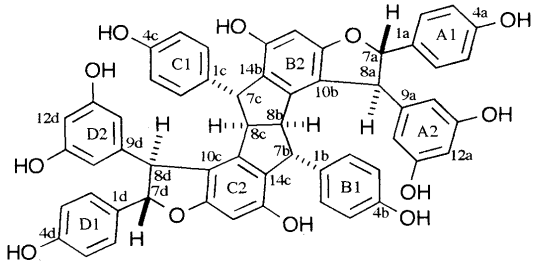

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Fig. 1

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data of Stenophyllols A—C (**11**—**13**)

No.	**11**		**12**		**13**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1a		130.6		134.6		134.6
2a(6a)	7.16 (d, 8.3)	139.2	6.89 (d, 8.8)	127.2	7.12 (d, 8.8)	127.2
3a(5a)	6.81 (d, 8.3)	116.5	6.76 (d, 8.8)	116.0	6.75 (d, 8.8)	116.0
4a		158.5		157.6		157.9[b]
7a	5.79 (d, 12.2)	88.5	5.84 (d, 3.9)	88.0	5.31 (d, 1.9)	93.8
8a	4.29 (br d, 12.2)	50.0	5.09 (d, 3.9)	52.5	4.32 (d, 1.9)	57.0
9a		142.4		141.4		148.6
10a		119.2		123.4	6.29 (br s)	148.6
11a		158.3		156.5		160.1
12a	6.60 (d, 2.0)	101.7	6.33 (d, 1.9)	101.3	6.32 (t, 1.9)	102.2
13a		157.6		158.1		160.1
14a	6.35 (br s)	106.8	6.26 (d, 1.9)	105.0	6.29 (br s)	106.6
1b		133.8		136.9		138.4
2b(6b)	6.81 (d, 8.5)	129.0	7.21 (d, 8.5)	130.0	6.75 (d, 8.8)	129.2
3b(5b)	6.55 (d, 8.5)	115.0	6.68 (d, 8.5)	115.8	6.57 (d, 8.8)	115.4
4b		155.8		156.1		155.9[b]
7b	5.46 (d, 4.4)	41.6	4.73 (d, 6.3)	51.9	4.30 (br s)	50.2
8b	3.92 (dd, 8.3, 4.4)	50.1	3.43 (br d, 6.3)	56.4	3.98 (br s)	60.5
9b		138.8		144.1		144.5
10b		118.1		120.6		116.2
11b		159.5		160.4		163.2
12b	5.81 (d, 2.2)	95.7	6.24 (d, 1.9)	95.9	6.21 (s)	96.7
13b		157.5		158.7		155.4
14b	5.29 (d, 2.2)	111.3	6.80 (br s)	106.8		126.5
1c		132.9		139.5		138.4
2c	7.53 (dd, 9.8, 2.0)	136.5	7.31 (d, 8.5)	129.9	6.75 (d, 8.8)	129.2
3c	6.22 (dd, 9.8, 2.0)	128.8	6.70 (d, 8.5)	115.8	6.57 (d, 8.8)	115.4
4c		187.7		156.2		155.9[b]
5c	6.17 (dd, 9.8, 2.0)	128.6	6.70 (d, 8.5)	115.8	6.57 (d, 8.8)	115.4
6c	7.17[a]	140.0	7.31 (d, 8.5)	129.9	6.75 (d, 8.8)	129.2
7c		136.5	5.37 (d, 9.8)	47.2		144.5
8c	4.63 (d, 8.3)	52.0	4.34 (dd, 9.8, 7.8)	53.5	3.98 (br s)	60.5
9c		139.0		150.8		144.5
10c		117.3		123.4		116.2
11c		159.8		154.6		163.2
12c	5.91 (d, 2.0)	96.1	6.08 (m)	102.3	6.21 (s)	96.7
13c		158.2		154.6		163.2
14c	5.22 (d, 2.0)	109.6	6.08 (m)	103.1		126.5
1d		130.5				134.6
2d(6d)	7.49 (d, 8.5)	130.4			7.12 (d, 8.8)	127.2
3d(5d)	6.89 (d, 8.5)	116.2			6.75 (d, 8.8)	116.0
4d		158.8				157.9[b]
7d	5.89 (d, 12.2)				5.31 (d, 1.9)	93.8
8d	4.58 (br d, 12.2)	51.3			4.32 (d, 1.9)	57.0
9d		139.1				148.6
10d		118.0			6.29 (br s)	106.6
11d		156.3				160.1
12d	6.40 (d, 1.9)				6.32 (t, 1.9)	102.2
13d		159.5				160.1
14d	6.58 (br s)	106.2			6.29 (br s)	106.6
OH	7.64, 7.82, 8.00, 8.38, 8.42, 8.50, 8.59, 8.71, 8.74		7.00, 7,96, 8.03 8.21, 8.31, 8.59		7.22, 7.88 8.28	

Measured in acetone-d_6. (^{1}H: 400 MHz; ^{13}C: 100 MHz). *a*) Obscured by overlapping with H-2a and H-6a. *b*) Interchangeable. All protons and carbons were assigned with the aid of ^{1}H–^{1}H, ^{1}H–^{1}H long-range, ^{13}C–^{1}H COSY and COLOC spectra.

A1, and H-8a had a correlation with H-14a on ring A2. In the COLOC spectrum, significant correlations were observed between C-2a(6a)/H-7a, C-8a/H-14a, C-9a/H-7a, C-11b/H-7a, C-10b/H-8a and C-10b/H-12b, respectively. These results indicated that resveratrol A (ring A1–C-7a–C-8a–ring A2) formed a dihydrobenzofuran ring with the B2 ring. On the other hand, ^{1}H–^{1}H long-range correlations were observed between H-7b/H-2b(6b), H-8b/H-14b and H-8a/H-8b, and there were ^{13}C–^{1}H long-range correlations between C-2b(6b), C-9a/H-7b, C-11a/H-7b, C-9b/H-7b and C-8b/H-14b, respectively. Therefore, the resvertrol B unit (ring B1–C-7b–C-8b–ring B2) was connected as shown in Fig. 2. The dimeric planar structure of resvertrol was drawn as the unit A. The structure of the remaining half-dimer unit was determined as follows. Through the ^{1}H- and ^{13}C-NMR spectra, including 2D techniques, the

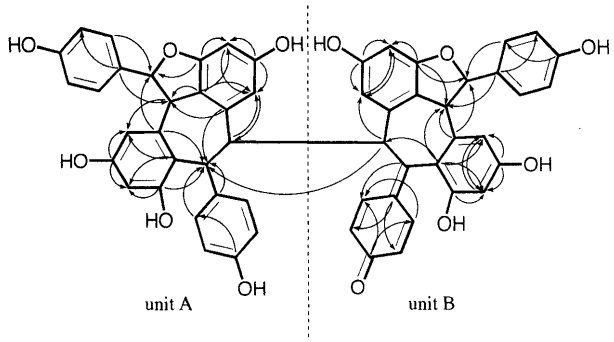

Fig. 2. Significant CH Long-range Correlations in the COLOC Spectrum ($J=8$ and 5 Hz)

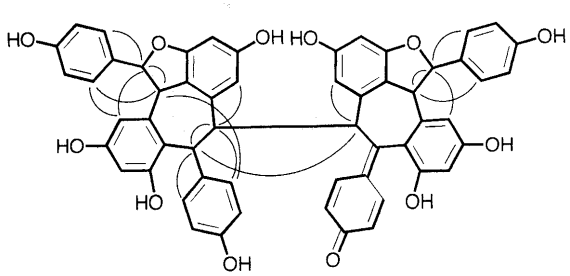

Fig. 3. NOE Interactions in the PSNOESY Spectrum of **11**

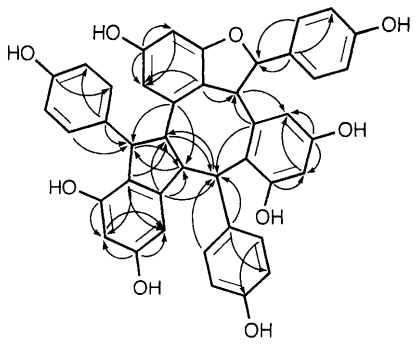

Fig. 4. CH Long-range Correltions in the COLOC Spectrum ($J=8$ Hz) of **12**

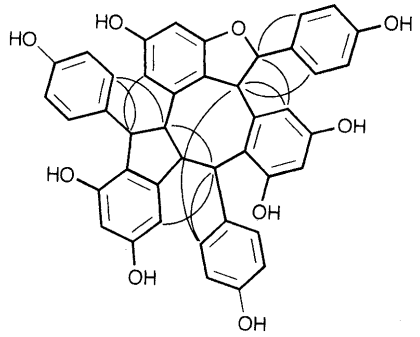

Fig. 5. Significant NOE Interactions in the PSNOESY Spectrum of **12**

presence of a 2,3-diarydihydrobenzofuran skeleton was proposed like unit A. However, four olefinic protons (H-2c, 3c, 5c and 6c) were observed in the ^{1}H-NMR spectrum, while the benzylmethine proton and the 4-hydroxyphenyl group disappeared. A carbonyl carbon (δ 187.7: C-4c) was correlated with two olefinic protons (H-2c and 6c) in the COLOC spectrum. A quaternary carbon at δ 136.5 (C-7c) was correlated with H-6c through ^3J. Taking into consideration the other correlations, the 4-hydroxyphenyl group was changed to a *para*-quinoid form (Fig. 2). H-8b in unit A and H-8c were mutually coupled in the ^{1}H-NMR spectrum, and C-8c was correlated with H-7b in the COLOC spectrum. The planar structure was thus drawn as in Fig. 2. In the phase-sensitive nuclear Overhauser and exchange spectroscopy (NOESY) spectrum, significant NOE interactions were observed (Fig. 3), which indicated that the relative configuration of **11** was the same as that of hopeaphenol (**10**). As **11** had an $[\alpha]_D$ of $-345°$, the structure of **11** was concluded to be an oxidative derivative of (−)-hopeaphenol (**10**).[5]

Compound **12** (stenophyllol B), a pale brownish solid, gave an $[M-H]^-$ ion peak at m/z 679 in the negative ion FAB-MS which corresponds to the molecular formula $C_{42}H_{32}O_9$ and is regarded as a stilbene trimer. The ^{1}H-NMR spectrum showed the presence of three sets of *ortho*-coupled aromatic protons assignable to three 4-hydroxyphenyl groups [δ 6.89 (2H, d, $J=8.8$ Hz, H-2a, 6a), 6.76 (2H, d, $J=8.8$ Hz, H-3a, 5a); 7.21 (2H, d, $J=8.5$ Hz, H-2b, 6b), 6.68 (2H, d, $J=8.5$ Hz, H-3b, 5b), 7.31 (2H, d, $J=8.5$ Hz, H-2c, 6c), 6.70 (2H, d, $J=8.5$ Hz, H-3c, 5c), three sets of protons assignable to 1,2,3,5-tetrasubstiuted benzene rings [δ 6.33 (1H, d, $J=1.9$ Hz, H-12a), 6.26 (1H, d, $J=1.9$ Hz, H-14a); 6.24 (1H, d, $J=1.9$ Hz, H-12b), 6.80 (1H, brs, H-14b); 6.08 (2H, m, H-12c and 14c)], a set of mutually coupled aliphatic methines [δ 5.84 (1H, d, $J=3.9$ Hz, H-7a), 5.09 (1H, d, $J=3.9$ Hz, H-8a)], a sequence of aliphatic methine protons coupled successively in this order [δ 4.73 (1H, d, $J=6.3$ Hz, H-7b), 3.43 (1H, br d, $J=6.3$ Hz, H-8b), 4.34 (1H, dd, $J=$ 9.8, 7.8 Hz, H-8c), 5.37 (1H, d, $J=9.8$ Hz, H-7c)] in addition to six phenolic hydroxyl groups (δ 7.00, 7.96, 8.03, 8.21, 8.31 and 8.59). All protonated carbon signals in the ^{13}C-NMR spectrum were assigned completely by the CH COSY spectrum and are listed in Table 1. In the ^{1}H–^{1}H long-range COSY spectrum, the mutually coupled methine protons (H-7a and H-8a) were correlated with H-2a(6a) and H-14a, respectively. ^{13}C–^{1}H long-range correlations were observed between C-2a(6a)/H-7a, C-8a/H-14a, C-9b/H-8a and C-9b/H-14b in the COLOC spectrum (Fig. 4). These results indicated that a resveratrol unit (ring A1–C-7a–C-8a–ring A2) formed a 2,3-arydihydrobenzofuran skeleton through ring B2. By detailed analysis of the ^{1}H–^{1}H long-range COSY and COLOC spectra (Fig. 4), the planar structure of **12** could be depicted as in Fig. 4. The relative stereochemistry was clarified by means of the phase sensitive nuclear Overhauser and exchange spectroscopy (PSNOES) spectrum (Fig. 5). As important NOE interactions were observed between H-7a/H-14a, H-8a/H-2a(6a), H-8a/H-2c(6c), H-7c/H-8b, H-8b/H-2b(6b), H-7b/H-14b and H-7c/H-14c, the relative stereochemistry was confirmed to be as in **12**. Previously, two resveratrol trimers with the same planar structure had been isolated from *Shorea disticha* (distichol)[6] and from *Stemonoporus canaliculatus* (canaliculatol)[7] (Dipterocarpaceae) (Fig. 6). Because of insufficient spectral data, their structures is not able to be proposed. In the case of distichol, it has been pointed out that the spectral data are very similar to those of the other resvertrol trimer

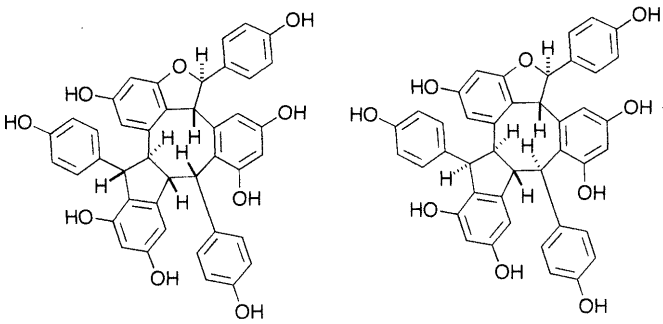

Fig. 6

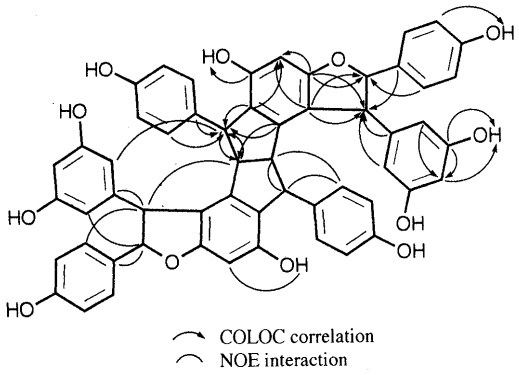

Fig. 7. CH Long-range Correlations in the COLOC Spectrum ($J=8$ Hz) and NOE Interactions in the PSNOESY Spectrum of **13**

(ampelopsin C) isolated from *Ampelopsis* (*A.*) *brevipendulata* var. *hancei* (Vitaceae).[8]

Compound **13** (stenophyllol C), a pale brownish solid, gave an $[M-H]^-$ ion peak at m/z 905 in the negative ion FAB-MS, corresponding to the molecular formula $C_{56}H_{42}HO_{12}$, which showed that **13** is a stilbene tetramer. The ^{1}H-NMR spectrum showed the presence of two sets of *ortho*-coupled aromatic protons assignable to two 4-hydroxyphenyl groups [δ 7.12, 6.75 (d, $J=8.8$ Hz); 6.75, 6.57 (d, $J=8.8$ Hz)], a 3,5-dihydroxyphenyl group [δ 6.29 (br s), 6.32 (t, $J=1.9$ Hz)], a singlet aromatic proton (δ 6.21), two broad aliphatic protons (δ 3.98 and 4.30) and two mutually coupled aliphatic hydrogens [δ 5.31 and 4.32 (d, $J=1.9$ Hz)] in addition to four phenolic hydroxyl groups (δ 6.29, 7.22, 7.88 and 8.28). In the ^{13}C-NMR spectrum, only 22 carbons signals were observed. Therefore, **13** had a symmetrical structure. All protonated carbons were assigned by the CH COSY spectrum and are listed in Table 1. The long-range correlations in the COLOC spectrum were as follows; δ_C 127.2/δ_H 5.31, δ_C 106.6/δ_H 4.32, δ_C 163.2/δ_H 5.31, δ_C 162.2/δ_H 4.32, δ_C 116.2/δ_H 5.31, δ_C 162.2/δ_H 4.32, δ_C 116.2/δ_H 6.21 and δ_C 163.2/δ_H 6.21. Thus, **13** had a 2,3-aryldihydrobenzofuran skeleton. Significant long-range correlations were further observed between two broadened aliphatic singlets (δ 4.30 and 3.98) (Fig. 7). The planar structure of **13** was thus determined to be a pallidol derivative,[9] in which two resveratrols are additionally coupled. The relative stereochemistry was deduced by means of the PSNOESY spectrum, in which NOE interactions were observed between H-7a/H-10a, H-8a/H-2a(6a), H-8a/H-8b and H-8b/H-2b(6b). The planar structure was the same as ampelopsin H isolated from *A. brevipedunculata* var. *hancei*.[10] However, **13** and ampelopsin H have different ^{1}H- and ^{13}C-NMR spectral data, and $[\alpha]_D$ values (**13**, $-66°$; ampelopsin H, $+105°$). Therefore **13** is concluded to be a stereoisomer of ampelopsin H.

Compounds **1**—**4** and **6**—**10** were identified to be (−)-4-hydroxymaackiain (**1**), sophoraflavanone G[11] (**2**), leachianone A[12] (**3**), sophoraflavanone I (**4**), sophoraflavanone H[3] (**6**), leachianone C[13] (**7**), (−)-ε-viniferin (**8**), davidiol B[14] (**9**) and (−)-hopeaphenol (**10**) by their spectral data and comparison with authentic samples.

Experimental

^{1}H- and ^{13}C-NMR spectra were recorded on JNM EX-400 (JEOL) spectrometers. Chemical shifts are shown as δ-values with tetramethylsilane (TMS) as the internal reference. Peak multiplicities are quoted in Hz. Negative ion FAB-MS was recorded on a JMS-DX-300 spectrometer equipped with a JMA 3500 data analysis system (JEOL). UV spectra were recorded on a UV-2200 spectrometer (Shimadzu), optical rotations on a DIP-370 (JASCO) instrument. Silica-gel 60 (70—230 mesh, Merck) and Sephadex LH 20 (Pharmacia) were used for column chromatography; Silica-gel 60H (Merck) was used for vacuum liquid chromatography (VLC); Kiesel-gel 60F_{254} (Merck) was used for analytical and preparative TLC.

Extraction and Isolation of Compounds (1—13) Dried and powdered roots of *S. stenophylla* (1 kg) collected in the U.S.A. in May 1995, were extracted with $(CH_3)_2CO$ at room temperature (5 L × 7) to give a dark brown gum (105 g). Part of the extract (80 g) was chromatographed on silica-gel (1.2 kg) eluting with an *n*-C_6H_{14}–$(CH_3)_2CO$ mixture. The *n*-C_6H_{14}–$(CH_3)_2CO$ (4:1) (15 g) fraction was further purified with silica-gel column chromatography and preparative TLC [both *n*-C_6H_{14}–$(CH_3)_2CO$ (3:1)] to give **1** (12 mg), **2** (200 mg), **3** (24 mg), **4** (80 mg), **6** (3 g), **7** (16 mg) and **8** (17 mg), respectively. The *n*-C_6H_{14}–$(CH_3)_2CO$ (2:1) fraction (10 g) was chromatographed on Sephadex LH 20 (acetone), and then purified by vacuum liquid chromatography eluting with $CHCl_3$–MeOH (3:1) and C_6H_6–$(CH_3)_2CO$ (3:1), and preparative TLC [$CHCl_3$–MeOH (3:1), C_6H_6–$(CH_3)_2CO$ (3:1) and C_6H_6–$(CH_3)_2CO$–MeOH–H_2O (6:2:3:0.2)] to give **5** (14 mg), **9** (35 mg), **10** (225 mg), **11** (1.35 g), **12** (46 mg) and **13** (27 mg), respectively.

Compound 5 (Sophoraflavanone I 7-*O*-β-Glucopyranoside) A colorless amorphous powder. Negative ion FAB-MS m/z: 811 ($[M-H]^-$), 649 (M−H−glucosyl moiety). UV λ_{max} (MeOH) nm: 221, 286, 340. $[\alpha]_D$ −173° (c= 0.07, MeOH). ^{1}H-NMR (acetone-d_6) δ: 1.45 (3H, s, Me, H-7″), 1.51 (3H, s, Me, H-6″), 1.59 (3H, s, Me, H-10″), 2.28 (2H, m, CH_2, H-4″), 2.60 (2H, t like m, CH_2, H-1″), 2.66 (1H, m, CH, H-2″), 2.78 (1H, dd, $J=16.9$, 3.2 Hz, H-3*eq*), 2.82—3.88 (m, sugar protons), 5.09 (1H, d, $J=6.9$ Hz, glucosyl anomeric proton, H-1‴), 3.09 (1H, dd, $J=16.9$, 12.8 Hz, H-3*ax*), 4.37 (1H, d, $J=6.9$ Hz, H-8‴), 4.44 (2H, br s, CH_2=, H-9″), 4.99 (1H, t like m, CH=, H-4″), 5.45 (1H, d, $J=6.9$ Hz, H-7‴), 5.68 (1H, dd, $J=12.8$, 3.2 Hz, H-2), 6.20 (2H, d, $J=2.0$ Hz, H-10‴, 14‴), 6.27 (1H, t, $J=2.0$ Hz, H-12‴), 6.29 (1H, s, H-6), 6.52 (1H, s, H-3′), 6.85 (2H, d, $J=9.0$ Hz, H-3‴, 5‴), 7.22 (2H, d, $J=9.0$ Hz, H-2‴, 6‴), 7.24 (1H, s, H-6′), 8.13 (2H, br s, OH × 2), 8.43, 8.90 (1H each, br s, OH), 12.18 (1H, s, C5-OH). ^{13}C-NMR (acetone-d_6) δ: flavanone moiety: 75.7 (C-2), 43.3 (C-3), 198.9 (C-4), 163.1 (C-5), 96.0 (C-6), 164.5 (C-7), 110.2 (C-8), 161.6 (C-9), 104.1 (C-10), 119.1 (C-1′), 155.8 (C-2′), 97.7 (C-3′), 162.1 (C-4′), 122.7 (C-5′), 124.1 (C-6′), 28.0 (C-1″), 47.8 (C-2″), 31.8 (C-3″), 124.6 (C-4″), 131.5 (C-5″), 25.9 (C-6″), 18.0 (C-7″), 149.0 (C-8″), 111.3 (C-9″), 19.0 (C-10″), 132.9 (C1‴), 128.3 (C-2‴, 6‴), 116.1 (C-3‴, 5‴), 158.3 (C-4‴), 94.4 (C-7‴), 57.7 (C-8‴), 145.8 (C-9‴), 107.3 (C-10‴, 14‴), 159.7 (C-11‴, 13‴), 102.3 (C-12‴); sugar moiety: 101.1 (C-1⁗), 74.7 (C-2⁗), 77.9 (C-3⁗), 71.3 (C-4⁗), 78.1 (C-5⁗), 62.6 (C-6⁗).

Compound 11 (Stenophyllol A) A yellow solid. Negative ion FAB-MS m/z: 903 ($[M-H]^-$). UV λ_{max} (MeOH) nm: 228, 285, 321, 400 sh. $[\alpha]_D$ −345° (c= 0.7, MeOH). ^{1}H- and ^{13}C-NMR spectral data are listed in Table 1.

Compound 12 (Stenophyllol B) A pale brownish solid. Negative ion FAB-MS m/z: 679 ($[M-H]^-$). UV λ_{max} (MeOH) nm: 208, 220 sh, 284, 325 sh. $[\alpha]_D$ −2° (c= 0.1, MeOH). ^{1}H- and ^{13}C-NMR spectral data are shown in Table 1.

Compound 13 (Stenophyllol C) A pale brownish solid. Negative ion FAB-MS *m/z*: 905 ($[M-H]^-$). UV λ_{max} (MeOH) nm: 210, 223 sh, 285, 330 sh. $[\alpha]_D$ $-66°$ ($c=0.1$, MeOH). ^{1}H- and ^{13}C-NMR spectral data are shown in Table 1.

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