Pergamon

PII: S0031-9422(97)00802-9

Phytochemistry, Vol. 48, No. 7, pp. 1187–1193, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

ISOFLAVONOIDS FROM *SOPHORA SECUNDIFLORA*, *S. ARIZONICA* AND *S. GYPSOPHILA*

TOSHIYUKI TANAKA, MASAYOSI OHYAMA, MUNEKAZU IINUMA,* YOSHIAKI SHIRATAKI,† MANKI KOMATSU† and CHARLES L. BURANDT‡

Department of Pharmacognosy, Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5 chome, Gifu 502, Japan; † Faculty of Pharmaceutical Sciences, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-02, Japan; ‡ Research Institute of Pharmaceutical Sciences, School of Pharmacy, The University of Mississippi, University, MS 38677, U.S.A.

(*Received in revised form* 26 *August* 1997)

Key Word Index—*Sophora secundiflora*; *S. arizonica*; *S. gypsophila*; Leguminosae; isoflavan; isoflavanone; pterocarpan.

Abstract—Eight new isoflavonoids, secundiflorols G–I and arizonicanols A–E, were isolated from the stem of *Sophora secundiflora* and the root of *S. arizonica* and *S. gypsophila* and the structures were determined by spectral analysis. The similarity of flavonoid occurrence was found in the three species. From the chemosystematic standpoint, the subgenus *Styphnologbium* seems to be composed of two chemical types (*S. secundiflora*, *S. arizonica*, and *S. gypsophila* vs *S. japonica* and *S. affinis*). © 1998 Elsevier Science Ltd. All rights reserved

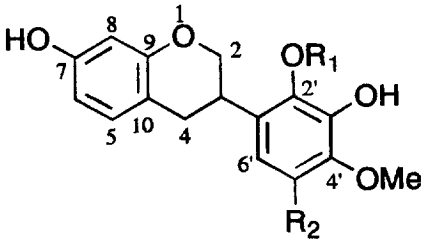
INTRODUCTION

In a previous chemosystematic study of the genus *Sophora* (Leguminosae) we have reported the isolation and structural determination of six new isoflavonoids, secundiflorols A–F, from the roots of *S. secundiflora* together with several known compounds [1, 2]. In the present paper, we now report the structures of three further new isoflavonoids, secundiflorols G–I, from the stem of *S. secundiflora*. The chemical constituents in the roots *S. arizonica* and *S. gypsophila*, which are members of the same subgenus *Styphnolobium* as *S. secundiflora*, were also examined and five new isoflavonoids, arizonicanols A–E, were isolated and characterized in addition to known compounds.

The acetone extract of the stem of *S. secundiflora* yielded three new compounds (**3**, **5** and **8**) in addition to 11 known compounds; one isoflavan (**1**), one pterocarpan (medicarpin), two 3-hydroxyisoflavanones [secondifloran (**12**) and secundiflorol A (**13**)], seven isoflavones [formononetin, genistein, prunetin, biochanin A, orobol, secundiflorol B (**14**) and secundiflorol C (**15**)], and one isoflavanone (secundiflorol F). From the acetone extract of *S. arizonica* ten compounds were isolated; three isoflavans (**2**–**4**), two isoflavanones (**6** and **7**), one pterocarpan (**9**), one caffeic acid ester mixture (**10**), and three isoflavones [derrone (**11**), **14** and **15**]. Five compounds (**3**, **4**, **6**, **7** and **9**) are new naturally occurring products. From the extract of *S. gypsophila* eight compounds were obtained; one isoflavan (**1**), three ptereocarpans (maackiain, medicalpin and **8**), two isoflavones (**14** and **15**), one flavanone (liquiritigenin) and one chalcone (isoliquiritigenin).

Compound **1**, a colourless powder, reacted positively to Gibbs reagent, and gave [M^+] at *m/z* 370 in the EIMS. In the ^{1}H NMR and HH COSY spectrum, a set of mutually coupled five protons [δ 2.81 (*br dd*, J = 16, 4 Hz), 2.95 (*dd*, J = 16, 11 Hz), 3.45 (*m*), 3.97 (*dd*, J = 11, 11 Hz) and 4.17 (*br d*, J = 11 Hz)] suggested the presence of a partial structure of [O]CH_2 CH[Ph]CH_2[Ph] assigned to H-4, H-3 and H-2 in an isoflavan skeleton. The ^{1}H NMR spectrum further exhibited the presence of two methoxyls (δ 3.80 and 3.81), two hydroxyls (δ 7.70 and 8.08) and an α,α-dimethylallyl group [δ 1.41 (6H, *s*, Me × 2), 4.93 (1H, *dd*, J = 18, 1 Hz, =CH_2), 4.95 (1H, *dd*, J = 11, 1 Hz, =CH_2) and 6.17 (1H, *dd*, J = 18, 11 Hz, =CH)] as well as an aromatic proton in singlet (δ 6.65), three protons in an ABC spin system [δ 6.30 (*d*, J = 2 Hz), 6.37 (*dd*, J = 8, 2 Hz) and 6.87 (*d*, J = 8 Hz)] (Table 1). Three prominent fragment ions were observed at *m/z* 123 (**1a**), 248 (**1b**) and 233 (**1c**) in the EIMS caused by the retro Diels Alder fragmentation and demethylation (Fig. 1), indicating that one of the hydroxyl groups was located in the A ring and that another hydroxyl, the two methoxyls and the α,α-dimethylallyl

* Author to whom correspondence should be addressed.



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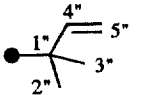

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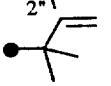

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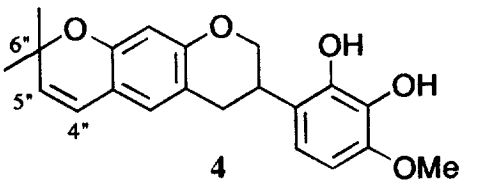

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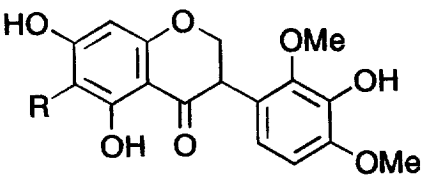

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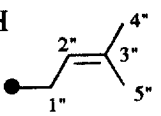
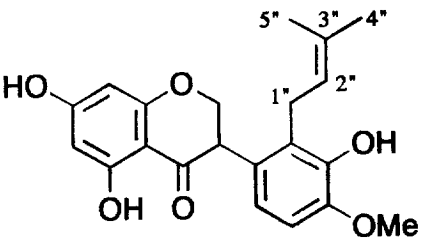
6: R =





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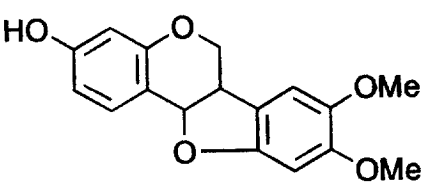

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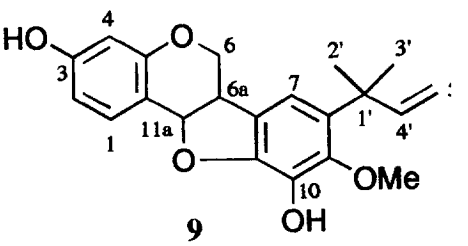

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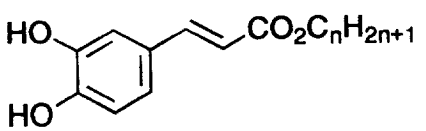

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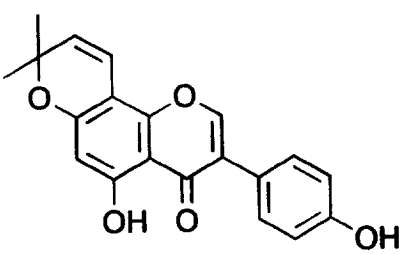

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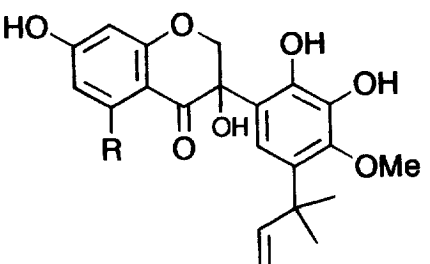
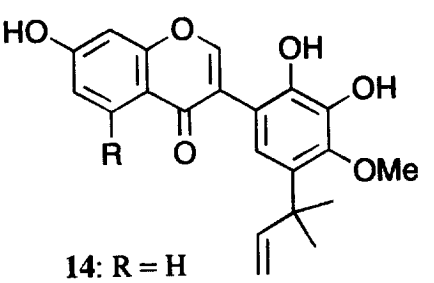


12: R = H
13: R = OH



14: R = H
15: R = OH

Table 1. ^{1}H NMR spectral data of compounds **1–9**

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	No.	**8**	**9**
2	3.97 (*dd*, 11, 117)	4.05 (*dd*, 10, 10)	3.98 (*dd*, 11, 11)	3.98 (*dd*, 11, 11)	4.43 (*dd*, 11, 6)	4.43 (*dd*, 11, 6)	4.48 (*t*, 11)	1	7.31 (*d*, 8)	7.29 (*d*, 8)
	4.17 (*br d*, 11)	4.32 (*br d*, 10)	4.26 (*br d*, 11)	4.26 (*br d*, 11)	4.53 (*dd*, 11, 11)	4.53 (*dd*, 11, 11)	4.50 (*dd*, 11, 7)	2	6.55 (*dd*, 8)	6.55 (*dd*, 8, 2)
3	3.45 (*m*)	3.51 (*m*)	3.50 (*m*)	3.49 (*m*)	4.25 (*dd*, 11, 6)	4.25 *dd*, 11, 6)	4.25 (*dd*, 11, 7)		6.35 (*d*, 2)	6.36 (*d*, 20
4	2.81 (*br dd*, 16, 4)	2.86 (*br dd*, 16, 4)	2.80 (*br dd*, 14, 3)	2.80 (*br dd*, 14, 3)				6	3.63 (*dd*, 11, 11)	3.58–3.62 (*m*)‡
	2.95 (*dd*, 16, 11)	2.98 (*dd*, 16, 11)	2.97 (*dd*, 14, 11)	2.98 (*dd*, 14, 3)					4.28 (*dd*, 11, 11)	4.28 (*m*)
5	6.87 (*d*, 8)	6.90 (*d*, 8)	6.89 (*d*, 8)	6.75 (*br s*)				6a	3.57 (*ddd*, 11, 6, 5)	3.58–3.62 (*m*)‡
6	6.37 (*dd*, 8, 2)	6.38 (*dd*, 8, 2)	6.36 (*dd*, 8, 2)		5.95 (*m*)*		5.97 (*br s*)†	7	7.02 (*s*)	6.81 (*s*)
8	6.30 (*d*, 2)	6.36 (*d*, 2)	6.28 (*d*, 2)	6.17 (*br s*)	5.95 (*m*)*	6.03 (*s*)	5.97 (*br s*)†	10	6.44 (*s*)	
5′			6.47 (*d*, 8)	6.48 (*d*, 8)	6.60 (*d*, 8)	6.68 (*d*, 8)	6.79 (*d*, 7)	11a	5.46 (*d*, 6)	5.49 (*d*, 7)
6′	6.65 (*s*)	6.60 (*s*)	6.62 (*br d*, 8)	6.62 (*d*, 8)	6.70 (*d*, 8)	6.63 (*d*, 8)	6.62 (*d*, 7)	2′,3′		1.41 (×2, *s*)
1″						3.26 (*br d*, 7)	3.51 (*br d*, 7)	4′		6.15 (*dd*, 18, 11)
2″	1.41 (*s*)	1.39 (*s*)				5.25 (*t* like *m*)	5.15 (*t* like *m*)	5′		4.92 (*dd*, 11, 1)
3″	1.41 (*s*)	1.39 (*s*)								4.94 (*dd*, 18, 1)
4″	6.17 (*dd*, 18, 11)	6.08 (*dd*, 18, 11)		6.31 (*d*, 10)		1.75 (*br s*)	1.75 (*br s*)	OMe	3.76 (*s*, C-8)	3.79 (*s*, C-9)
5″	4.93 (*dd*, 18, 1)	4.95 (*dd*, 18, 1)		5.55 (*d*, 10)		1.64 (*br s*)	1.67 (*br s*)		3.75 (*s*, C-9)	
	4.95 (*dd*, 11, 1)	4.97 (*dd*, 11, 1)		3.80 (*s*, C-4′)				OH	8.54 (C-3)	7.73, 8.57 (*s*)
OMe	3.81 (*s*, C-4′)	3.75 (*s*, C-4′)	3.80 (*s*, C-4′)		3.83 (*s*, C-2′)	3.84 (*s*, C-2′)				
	3.80 (*s*, C-2′)				3.84 (*s*, C-4′)					
OH	7.70 (*s*, C-3′)	5.73, 5.79	7.43, 7.71	7.41, 7.66 (*s*)	8.00, 9.91 C-7, 3′)	7.57, 9.50 (C-7, 3′)	7.44, 9.59 (C-7, 3′)			
	8.08 (*s*, C-7)	5.84 (*s*)	8.12 (*s*)		12.35 (*s*, C-5)	12.64 (*s*, C-5)	12.31 (*s*, C-5)			
Me				1.37 (×2, C-6″)						

Compounds **1** and **3–9** were measured in acetone-d_6, and **2** was measured in $CDCl_3$.
*–‡: overlapped.

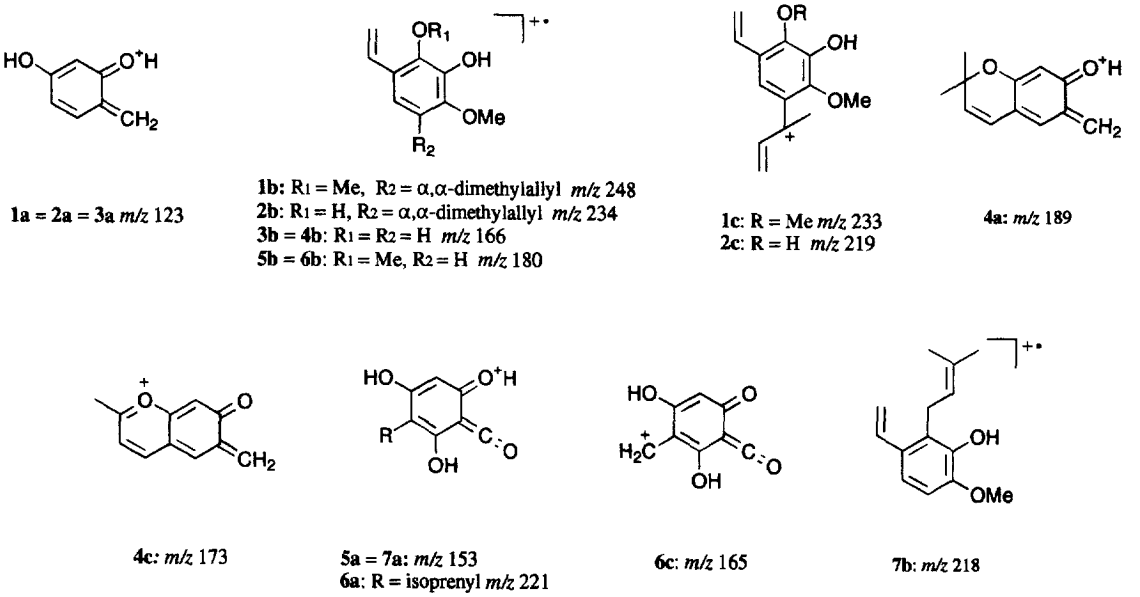


Fig. 1. Prominent fragment ions of **1**–**7** in EIMS.

groups were in the B ring. An NOE was observed at H-4 in the difference NOE when the *ortho*-coupled aromatic proton (δ 6.87) was irradiated, which supported that the hydroxyl group in the A ring was at C-7. Other NOEs were observed at H-2, H-3 and H-4 in the experiment when the aromatic proton (δ 6.65) assignable to H-6′ in the B ring was irradiated (Fig. 2), supporting that the B ring had a 2′,3′,4′,5′-tetrasubstituted pattern. The other NOEs observed in the experiment are shown in Fig. 2. Thus, the B ring moiety has a 5′-α,α-dimethylallyl-3′-hydroxy-2′,4′-dimethoxyl substitution. Consequently the structure of **1** was concluded to be 5′-α.α-dimethylallyl-7,3′-dihydroxy-2′,4′-dimethoxyisoflavan, unaniisoflavan, which has already been isolated from the same plant [3], the assignment of the ^{13}C NMR spectrum (Table 2) was accomplished in this study.

Compound **2**, a pale yellow oil, gave [M^+] at *m/z*

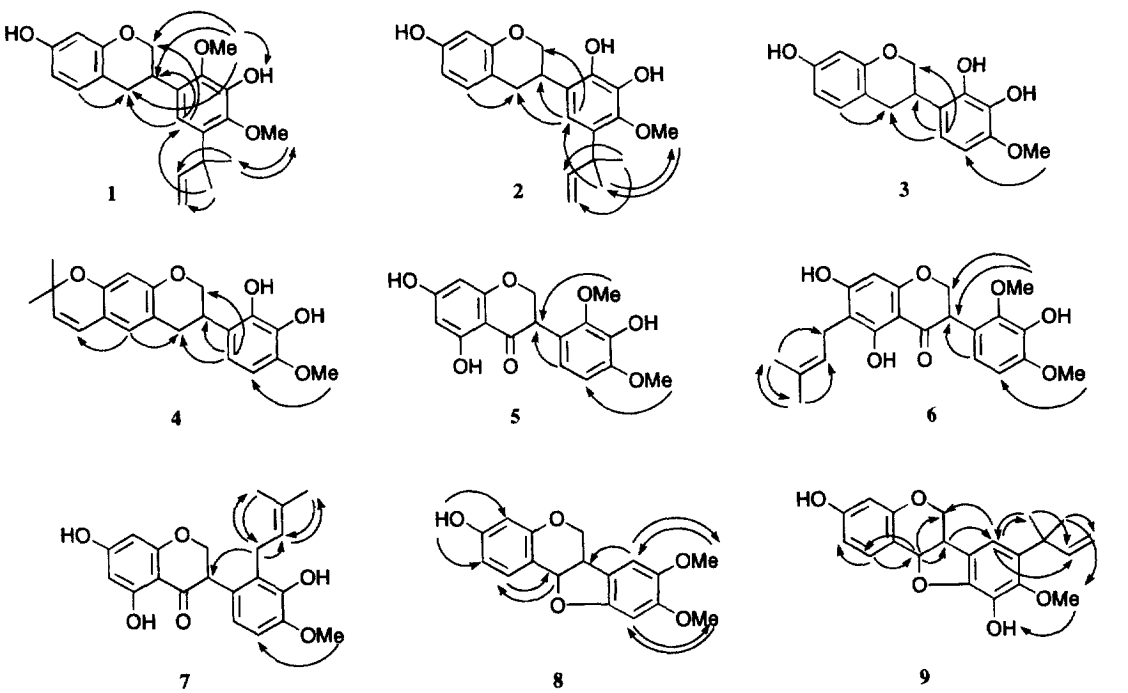


Fig. 2. NOE interactions in the difference NOE of **1**–**9**.

Table 2. ^{13}C NMR spectral data of compounds **1–9**

Carbon no.	1	2	3	4	5	6	7	Carbon no.	8	9
2	70.0	69.6	70.4	70.5	71.4	71.3	72.2	1	133.0	133.1
3	32.2	32.7	33.0	33.0	48.1	47.8	48.0	2	110.4	110.3
4	30.7	30.8	31.0	31.0	198.2	198.1	198.0	3	159.5	159.7
5	130.2	130.3	131.0	122.7	165.7	162.0	165.6	4	103.8	103.9
6	108.5	108.1	108.7	121.1	96.9	106.6	96.9	4*	157.6	157.7
7	154.3	155.0	157.5	153.2	169.1	162.5*	167.2	6	67.0	67.0
8	104.4	103.2	103.7	104.5	95.6	94.9	96.5	6*	41.2	41.5
9	154.2	154.9	156.1	156.0	164.5	164.1*	164.4	6†	118.3	122.7
10	114.1	114.4	114.3	115.6	103.4	103.2	103.8	7	118.3	113.5
1′	116.1	122.3	121.8	121.6	122.1	122.2	128.0†	8	144.8	134.5*
2′	144.5	142.1	144.3	144.3	146.8	146.6	128.1†	9	151.6	150.1
3′	134.4	132.5	134.2	134.3	140.3	140.1	145.1	10	96.6	136.0*
4′	149.7	145.7	147.7	147.7	149.4	149.1	147.2	10*	154.9	147.7
5′	137.7	136.9	103.6	103.8	107.3	107.3	109.8	11*	78.9	79.5
6′	116.6	116.8	117.8	117.8	120.4	120.2	120.1	11†	113.0	112.8
1″	40.2	40.4				21.5	25.8‡	1′		41.1
2″	27.8	28.2				123.4	124.1	2′		28.6
3″	27.8	28.1				131.0	131.6	3′		28.7
4″	148.6	148.6		117.9		25.6	25.8‡	4′		150.2
5″	110.0	109.8		129.8		17.6	14.4	5′	56.2	109.7
OMe	60.8	60.7	56.3	56.3	56.5	56.3	56.2	OMe	56.2	60.1
	60.9				60.1	60.0			57.3	
6″-Me				28.0 (×2)						

Compounds **1** and **3–9** were measured in acetone-d_6, and **2** was measured in $CDCl_3$.
*–†: interchangeable in a same column.
‡: overlapped.

356 and reacted positively to both Gibbs and $FeCl_3$ tests. All spectral data (UV, ^1H and ^{13}C NMR) were closely similar to those of **1**. based on prominent fragments in EIMS [*m/z* 123 (**2a**), 234 (**2b**), and 219 (**2c**)] and the ^1H NMR spectral data, the isoflavan B ring had two hydroxyls, a methoxyl and an α,α-dimethylallyl group. In the NOE experiment, NOEs were observed between the methoxyl and the α,α-dimethylallyl group as shown in Fig. 2. These results indicated that the B ring moiety of **2** had a 5′-α.α-dimethylallyl-2′,3′-dihydroxy-4′-methoxyl substitution. The structure was thus determined as 5′-α.α-dimethylallyl-7,2′,3′-trihydroxy-4′-methoxyisoflavan, named secundiflorol G.

Compound **3**, a colourless solid, gave [M^+] at *m/z* 288 in the EIMS and gave positive Gibbs and $FeCl_3$ tests. It had the same isoflavan skeleton as **1**. On the basis of the ^1H NMR spectrum and two significant fragments at *m/z* 123 (**3a**) and 166 (**3b**) in the EIMS Fig. 1, one of hydroxyls was located in the A ring, and two hydroxyls and the methoxyl group in the B ring. The correlations observed in the difference NOE experiment are drawn in Fig. 2. The results substantiated the structure of **3** as 7,2′,3′-trihydroxy-4′-methoxyisoflavan, named arizonicanol A.

Compound **4**, a colourless powder, gave [M^+] at *m/z* 354 in EIMS, and a positive Gibbs reagent. The ^1H NMR spectrum suggested that **4** was also an isoflavan which had one methoxyl (δ 3.80), three hydroxyl groups (δ 7.41 and 7.66). The ^1H NMR spectrum further exhibited the presence of two aromatic protons in a singlet (δ 6.17 and 6.75), a set of two *ortho*-coupled protons [(δ 6.48 and 6.62 (each *d*, $J = 8$ Hz)] and one ring [δ 5.55, 6.31 (1H each, *d*, $J = 10$ Hz) and 1.37 (6H, Me × 2)]. The EIMS fragment ions at *m/z* 189 (**4a**), 166 (**4b**) and 173 (**4c**) (Fig. 1) showed that the dimethylchromene ring was fused at the A ring and that two hydroxyls and the methoxyl group were located on the B ring. Comparison of ^1H and ^{13}C NMR spectral data of **4** including NOE experiments with those of **3** indicated that the B ring of **4** was the same as that of **3**. Two singlets (δ 6.17 and 6.75) assigned to H-8 and H-5 indicated that the dimethylchromene was fused at the A ring in a linear form, which was further confirmed by NOE experiments in Fig. 2. Therefore the structure of **4** was concluded to be 2′,3′-dihydroxy-4′-methoxy-[6″,6″-dimethylpyrano(2″,3″:7,6)]isoflavan, named arizonicanol B.

Compound **5**, a colourless amorphous powder, gave [M^+] at *m/z* 332 in EIMS, and reacted positively to Gibbs and $FeCl_3$ tests. The UV spectrum absorption bands (230 *sh*, 288 and 335 *sh* nm) suggested that **5** was either a flavanone or an isoflavanone, however the ^1H NMR spectrum showed a set of mutually coupled

three protons [δ 4.43 (*dd*, J = 11, 6 Hz, H-2), 4.53 (*dd*, J = 11, 11 Hz, H-2) and 4.25 (*dd*, J = 11, 6 Hz, H-3), clarifying that **5** had an isoflavanone skeleton. The presence of three hydroxyls [δ 8.00, 9.91 and 12.35 (chelated)] and two methyl groups was supported by the ^{1}H NMR spectrum and significant fragment ions [*m/z* 153 (**5a**) and 180 (**5b**)]. Two hydroxyl groups were located in the A ring and a hydroxyl and two methoxyl groups in the B ring. In the ^{1}H NMR spectrum, the chelated hydroxyl group was assigned to that of C-5. Three quaternary carbon signals occupied by an oxygen function (δ 164.5, 165.7 and 169.1) in the ^{13}C NMR spectrum showed that the A ring had a phloroglucinol oxidation pattern with a 5,7-dihydroxyl substitution. A set of *ortho*-coupled protons (δ 6.60 and 6.70) and three quaternary carbon signals attached to an oxygen function (δ 140.3, 146.8 and 149.4) in the ^{13}C NMR spectrum, indicated that B ring oxygenation pattern corresponded to pyrogallol with a 2′,3′,4′-trisubstitution pattern. The chemical shifts of the methoxyl groups at δ 56.5 and 60.1 showed that both *ortho*-positions of the A ring were unsubstituted while in the B ring both *ortho*-positions were substituted. When the methoxyl groups were irradiated, NOEs were observed as shown in Fig. 2 and the B ring moiety was shown to have a 3′-hydroxy-2′,4′-dimethoxyl substitution. Thus, the structure of **5** was characterized as 5,7,3′-trihydroxy-2′,4′-dimethoxy-isoflavanone, and was named secundiflorol H.

Compound **6**, a colourless amorphous powder, gave [M$^+$] at *m/z* 400 in EIMS and reacted positively to Gibbs and $FeCl_3$ tests. IR absorption at 1650 cm^{-1} suggested the presence of a carbonyl group, UV absorption at 292 nm and the ^{1}H NMR spectral data (Table 1) indicated that **6** was an isoflavanone. Comparison of a fragment (**6b**) in the EIMS, ^{1}H NMR including NOE experiments (Fig. 2), and ^{13}C NMR spectral data with those of **5** indicated that the B ring moiety had the same substitution as that of **5**. Other fragments [*m/z* 221 (**6a**) and 165 (**6c**)], ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2) showed that **5** had a 5,7-dihydroxyl substitution in the A ring and a γ,γ-dimethylallyl group was located at C-6 or C-8. The chelated hydroxyl group (δ 12.64) was shifted in a lower field by 0.29 ppm compared with that of **6**, indicating that the γ,γ-dimethylallyl group was substituted at C-6. The structure of **6** was concluded to be 6-γ,γ-dimethylallyl-5,7,3′-trihydroxy-2′,4′-methoxyisoflavanone, named arizonicanol C.

Compound **7**, a colourless oil, gave [M$^+$] at *m/z* 370 in EIMS and positive Gibbs and $FeCl_3$ tests. it is an isoflavanone derivative with three hydroxyls, one methoxyl and one γ,γ-dimethylallyl group. Prominent EIMS fragments [*m/z* 153 (**7a**) and 218 (**7b**)] showed that **7** had two hydroxyl groups in the A ring, while one hydroxyl, the methoxyl and the γ,γ-dimethylallyl group were substituted in the B ring. ^{1}H and ^{13}C NMR spectral data indicated that the A ring had a 5,7-dihydroxyl substitution. A methylene carbon (C-1″) observed at δ 25.8 in the ^{13}C NMR spectrum showed that both *ortho*-positions were substituted with an oxygen and/or another substituent [4]. As an NOE was observed at H-3 when H-1″ irradiated, the γ,γ-dimethylallyl group was located at C-2′. One of the *ortho*-coupled protons (δ 6.79) caused an NOE interaction with the methoxyl group (Fig. 2). These results showed that the B ring had a 2′-γ,γ-dimethylallyl-3′-hydroxy-4′-methoxyl substitution. Thus, **7** was characterized as 2′-γ,γ-dimethylallyl-5,7,3′-trihydroxy-4′-methoxy-isoflavanone, named arizonicanol D. This is a very unusual B ring substitution and to the best of our knowledge, secundiflorol F [2] is the first example.

Compound **8**, a colourless solid, gave [M$^+$] at *m/z* 300 in the EIMS. Absorption bands at 226, 275 *sh*, 287, 295 *sh* nm were observed in the UV spectrum. In the ^{1}H NMR spectrum including HH COSY spectrum, a set of mutually coupled four protons [δ 3.63 (*dd*, J = 11, 11 Hz), 4.28 (*dd*, J = 11, 4 Hz), 3.57 (*ddd*, J = 11, 6, 5 Hz) and 5.46 (*d*, J = 7 Hz)] were assignable to H-6, H-6a and H-11a in a pterocarpan skeleton. The presence of a hydroxyl and two methoxyl groups was also exhibited in the ^{1}H NMR spectrum in addition to two aromatic protons in a singlet and three aromatic protons in an ABX spin system (Table 1). The NOEs observed are depicted in Fig. 2. From these results, the structure of **8** was determined to be 3-hydroxy-8,9-dimethoxypterocarpan, named secundiflorol I.

Compound **9**, a colourless solid, gave the [M$^+$] at *m/z* 354 in EIMS and reacted positively to Gibbs reagent. The compound was also a pterocarpan derivative with two hydroxyls, one methoxyl and one α,α-dimethylallyl group. NOEs were observed as shown in Fig. 2. Thus, the structure of **9** was characterized as 8-α,α-dimethylallyl-3,10-dihydroxy-9-methoxypterocarpan, named arizonicanol E.

The three species *S. secundiflora*, *S. arizonica* and *S. gypsophila* belong to the subgenus *Styphnolobium* [5, 6]. The flavonoids isolated from above these species were closely similar except for the absence of secondifloran (**12**) and secundiflorol A (**13**) in *S. arizonica* and *S. gypsophila*. The flavonoids isolated from the above three *Sophora* species have generally a 2′,3′,4′-trioxygenated B ring and a prenyl moiety as a γ,γ-dimethylallyl or an α,α-dimethylallyl group, in the A or B ring. *Sophora japonica* and *S. affinis* which are also classified in the same subgenus had flavonoids with fundamentally different oxygenation patterns and no prenylation [5]. Thus, from the chemosystematic standpoint, the subgenus *Styphnolobium* may be divided into two chemical types.

EXPERIMENTAL

Plant materials

Stems of *Sophora secundiflora* (Ort.) DC were collected at Kingsville, Kleberg. Co., Texas, U.S.A. in August 1993. Roots of *S. arizonica* Wats. were col-

lected from Mohave, Arizona, U.S.A. in May, 1994 and those of *S. gypsophila* B. L. Turner from Edo. Chihuahua, Mexico in May, 1994. Voucher specimens, Dr Burandt No. 2535, 2616 and 2617, have been deposited in the private herbarium of the collector.

Extraction and isolation

The air-dried and powdered plant tissues (each 900 g) were extracted with Me_2CO (3 l × 3) at room temp. and the solutions concentrated *in vacuo*. The extract of the stem of *S. secudiflora* (35 g) was chromatographed on silica gel (1 kg) eluted with a hexane–Me_2CO mixture. The frs containing flavonoids were further purified by Sephadex LH-20 CC (solvent: MeOH or Me_2CO), vacuum liquid chromatography (solvent system: hexane–Me_2CO–EtOAc, 4:1:1), prep. TLC (solvent systems: $CHCl_3$–MeOH, 10:1 and benzene–Me_2CO–EtOAc, 8:1:1) and recryst. to give 15 pure compounds [**1** (15 mg), **3** (35 mg), **5** (8 mg), **8** (9 mg), medicalpin (320 mg), **12** (8 mg), **13** (5 mg), formononetin (52 mg), genistein (9 mg), biochanin A (3 mg), prunetin (5 mg), orobol (8 mg), **14** (13 mg), **15** (10 mg) and secundiflorol F (3 mg)]. The Me_2CO extracts of *S. arizonica* (65 g) and *S. gypsophila* (47 g) were separated in the same manner as that of *S. secundiflora*. The extract of *S. arizonica* gave 10 compounds [**2** (412 mg), **3** (55 mg), **4** (11 mg), **6** (8 mg), **7** (10 mg), **9** (17 mg), **10** (120 mg), **11** (4 mg), **14** (8 mg) and **15** (17 mg)]. The extract of *S. gypsophila* gave eight compounds [**1** (270 mg), maackiain (120 mg), medicalpin (435 mg), **8** (6 mg), **14** (9 mg), **15** (3 mg), liquiritigenin (11 mg) and isoliquiritigenin (23 mg)].

Compound **1** (*unaniisoflavan*). A colourless powder. UV λ_{max}^{MeOH}: 220, 286, IR (KBr, cm^{-1}): 3350, 2950, 1620, 1953, 1510, EIMS *m/z* (rel. int.): 370 (100), 248 (55), 133 (13), 123 (18).

Compound **2** (*secundiflorol G*). A yellow oil. UV λ_{max}^{MeOH}: 285, 295 *sh*, EIMS *m/z* (rel. int.): 356 (100), 234 (36), 219 (21), 123 (30).

Compound **3** (*arizonicanol A*). A colourless solid. UV λ_{max}^{MeOH}: 229, 283, 293 *sh*, 325 *sh*, EIMS *m/z* (rel. int.): 288 (100), 166 (77), 154 (33), 123 (46).

Compound **4** (*arizonicanol B*). A colourless powder. UV λ_{max}^{MeOH}: 257, 275 *sh*, 317, IR (KBr, cm^{-1}): 3450, 2900, 1618, 1570, 1510, EIMS *m/z* (rel. int.): 354 (28), 339 (100), 166 (3), 189 (7), 173 (11).

Compound **5** (*secundiflorol H*). A colourless amorphous powder. UV λ_{max}^{MeOH}: 230 *sh*, 288, 335 *sh*, EIMS *m/z* (rel. int.): 332 (100), 180 (97), 153 (90).

Compound **6** (*arizonicanol C*). A colourless amorphous powder. UV λ_{max}^{MeOH}: 292, IR (KBr, cm $^{-1}$): 3400, 2900, 1650, 1620, 1500, EIMS *m/z* (rel. int.): 400 (100), 383 (11), 345 (25), 221 (96), 180 (53), 165 (98).

Compound **7** (*arizonicanol D*). A colourless oil. UV λ_{max}^{MeOH}: 230 *sh*, 289, 330 *sh*, EIMS *m/z* (rel. int.): 370 (98), 314 (52), 218 (23), 191 (100), 153 (90), 143 (40).

Compound **8** (*secundiflorol I*). A colourless solid. UV λ_{max}^{MeOH}: 226, 275 *sh*, 287, 295 *sh*, EIMS *m/z* (rel. int.): 300 (100).

Compound **9** (*arizonicanol E*). A colourless solid. UV λ_{max}^{MeOH}: 226, 280, 285, 321, EIMS *m/z* (rel. int.): 354 (100), 339 (15).

Compound **10**. A colourless solid. EIMS *m/z* (rel. int.): 516 (5), 488 (12), 460 (40), 432 (49), 180 (100), 163 (48), ^{1}H NMR (Me_2CO-d_6) δ: 0.89 (Me), 1.30 (CH_2), 4.14 (*t*, J = 7 Hz, OCH_2), 6.27 (*d*, J = 16 Hz, *trans*-olefinic proton), 6.86 (*d*, J = 8 Hz, H-6), 7.03 (*dd*, J = 8, 1 Hz, H-5), 7.15 (*d*, J = 1 Hz, H-2), 8.30 (*br s*, OH).

Compound **11** (*derrone*). A pale yellow amorphous powder. UV λ_{max}^{MeOH}: 269, 305 *sh*, 350 *sh*. EIMS *m/z* (rel. int.): 336 (22), 321 (100). ^{1}H NMR (Me_2CO-d_6) δ: 1.48 (6H, *s*, Me × 2), 5.75 (1H, *d*, J = 10 Hz, H-4), 6.20 (1H, *s*, H-6), 6.72 (1H, *d*, J = 10 Hz, H-3″), 6.91 (2H, *d*, J = 9 Hz, H-3′, 5′), 7.46 (2H, *d*, J = 9 Hz, H-2′, 6′), 8.25 (1H, *s*, H-2), 8.2 (1H, *br s*, C-4-OH), 13.12 (1H, *s*, C-5-OH).

Acknowledgment—A part of this work was financially supported by the San-Ei Gen Foundation for Food Chemical Research.

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