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FIVE RESVERATROL OLIGOMERS FROM ROOTS OF *SOPHORA LEACHIANA*

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Key Word Index—*Sophora leachiana*; Leguminosae; roots; oligostilbenoids; leachianols C–G; structural elucidation.

Abstract—Five novel oligostilbenes, named leachianols C–G, were isolated from the roots of *Sophora leachiana*. Their structures were established by means of 2D NMR spectroscopic analysis, including HMBC, COLOC and PSNOESY, to be a resveratrol tetramer with a 2-cyclohexen-4-one ring (leachianol C), a resveratrol trimer with a dihydrobenzofuran ring (leachianol D), a regioisomer of leachianol D (leachianol E), a resveratrol dimer (leachianol F) and a stereoisomer of leachianol F (leachianol G), respectively. These oligostilbenes in *S. leachiana* derived from pallidol are different from those in *S. moorcroftiana*, which are derived from ε-viniferin.

INTRODUCTION

In our previous studies on the chemical constituents of *Sophora leachiana* Peck., the structures of characteristic oligostilbenes [1,2] condensed with a resveratrol and a pallidol [3,4], and flavanones with a lavandulyl group [4] were classified. A detailed chemical analysis of the roots has resulted in the isolation of five novel resveratrol oligomers (**1**–**5**), named leachianols C–G. The structural elucidation of these oligomers is discussed in this paper.

RESULTS AND DISCUSSION

An ethylacetate-soluble portion (15 g) in the acetone extract (60 g) of *S. leachiana* roots (580 g) was repeatedly subjected to column chromatography on silica gel (benzene–acetone system, gradient), Sephadex LH-20 (methanol, or acetone–water, 4:1), and vacuum liquid chromatography using silica gel 60H (chloroform–methanol, 10:1) to afford **1**–**5**.

Leachianol C (**1**) [2], obtained as a brown solid, showed a $[M - H]^-$ ion at m/z 907 in the negative ion FAB mass spectrum consistent with the molecular formula $C_{56}H_{44}O_{12}$ and with a resveratrol tetramer. The ^1H NMR spectrum (Table 1) showed (i) six sets of *ortho*-coupled aromatic protons based on three 4-hydroxyphenyl groups, (ii) aromatic protons in an AX_2-system [H-10″(14″) and H-12″] and a multiplet consisting of three aromatic protons [H-10‴(14‴) and H-12‴] based on two 3,5-dihydroxyphenyl groups, (iii) two aromatic methine protons in a 1,2,3,5-tetrasubstituted benzene (H-12 and H-14), (iv) three sets of mutually coupled aliphatic protons (H-8–H-8′, H-5″*ax*–5″*eq* and H-7‴–H-8‴), (v) a set of olefinic methine protons (H-2″–H-3″) and (vi) seven aliphatic methine protons (H-7, H-7′, H-6″, H-7″, H-8″, H-12″ and H-14″), in addition to nine hydroxyl protons. The absorption bands at 1720 and 1670 cm^{-1} in the IR spectrum, and the carbon signals at δ_C 194.1, 194.5 and 206.0 in the ^{13}C NMR spectrum indicated the presence of two unsaturated carbonyl groups and an isolated one. The ^1H–^1H long-range COSY, COLOC (Fig. 1) and the HMBC spectrum suggested that **1** had the same partial structure **1a** (Fig. 2) as leachianol A, isolated previously from this species [1]; the moiety originated from a pallidol molecule.

The ^1H–^1H long-range COSY spectrum showed that one of the methylene protons at δ_H 2.50 and a vicinal aliphatic methine proton at δ_H 3.27 were correlated to olefinic protons at δ_H 4.84 and 4.74 assigned to the α- and β-position in the α,β-unsaturated ketone group, respectively, which indicated the presence of a 2-cyclohexen-4-one ring transformed from the 4-hydroxyphenyl group in a resveratrol molecule. The ^1H–^1H COSY spectrum showed a sequence of aliphatic methine protons coupled successively [δ_H 3.21 (*m*), 3.25 (*m*), 3.57 (*t*, $J = 10$ Hz) and 3.35 (*d*, $J = 10$ Hz)], which had cross-peaks with carbons at δ_C 62.1, 55.6, 62.2 and 65.8, respectively, in the ^{13}C–^1H COSY spectrum. The long-range correlations via ^3J were observed between the following signals: δ_C 158.5–δ_H 3.21; δ_C 55.6–δ_H 6.63; δ_C 62.2–δ_H 6.07 in the COLOC spectrum and those via ^2J were δ_H 3.35–δ_C 133.4; δ_H 3.35–δ_C 47.2 in the HMBC spectrum indicating that the remaining partial structure can be drawn as **1b** (Fig. 2).

Finally, the long-range correlations between δ_C 47.2 (C-1″)–δ_C 3.08 (H-12′), δ_C 47.2 (C-1″)–δ_H 3.48 (H-14′),

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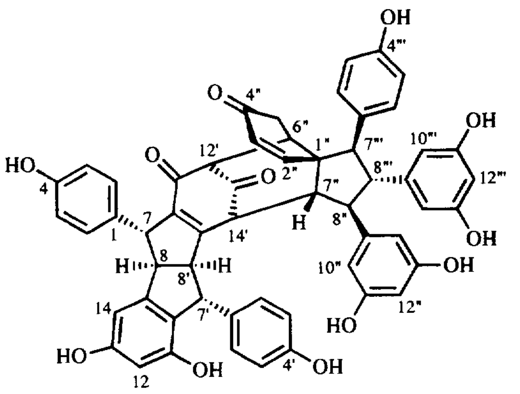

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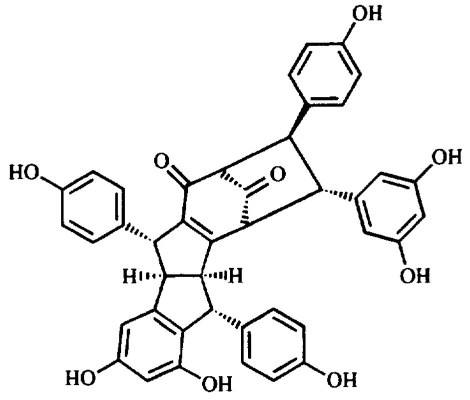
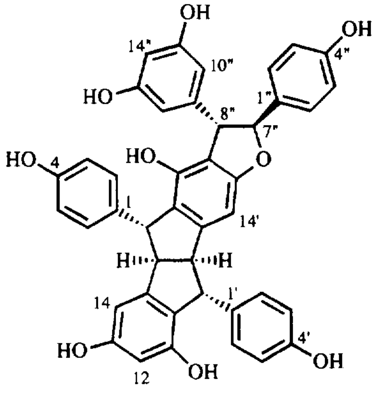


leachianol A



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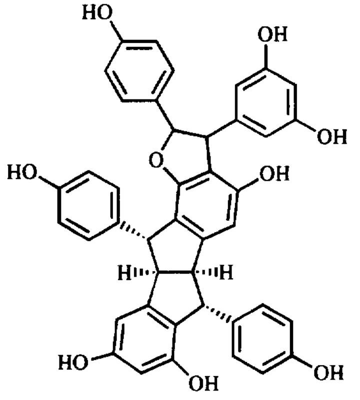

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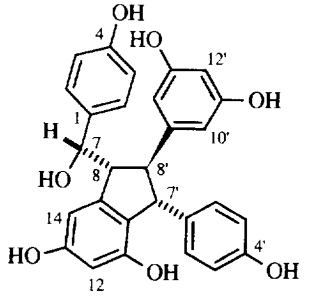

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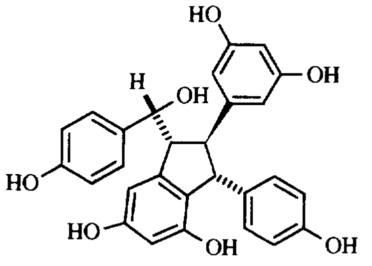

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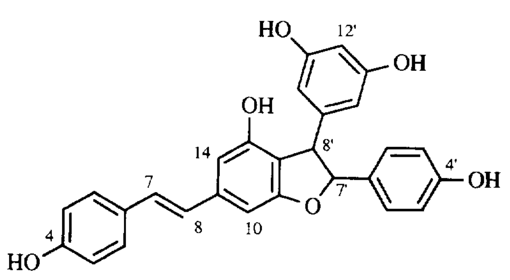

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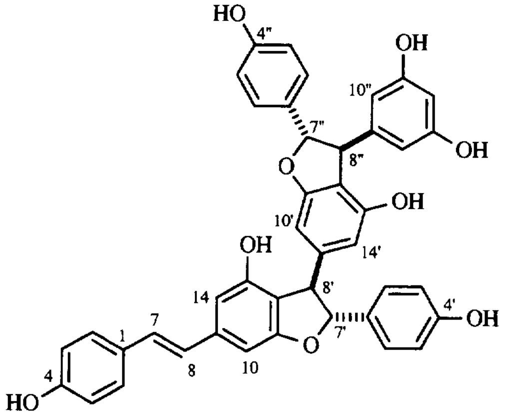

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Table 1. ^{1}H and ^{13}C NMR data of leachianol C(**1**) in acetone -d_6

No.	δ_H	δ_C	No.	δ_H	δ_C
1		134.2 (*s*)	1″		47.2 (*s*)
2(6)	6.97 (*d*, 8)	129.4 (*d*)	2″	4.74 (*d*, 10)	158.5 (*d*)
3(5)	6.66(*d*, 8)	116.3 (*d*)	3″	4.84 (*d*, 10)	126.7 (*d*)
4		157.2 (*s*)	4″		194.5 (*s*)
			5″	2.50 (*d*, 18) 2.94 (*dd*, 18.6)	38.1 (*t*)
			6″	3.27 (*m*)^a	51.5 (*d*)
7	3.98 (*br s*)	52.9 (*d*)	7″	3.21 (*m*)^a	62.1 (*d*)
8	3.72 (*d*, 5)	58.5 (*d*)	8″	3.25 (*m*)^a	55.6 (*d*)
9		150.2 (*s*)	9″		143.4 (*s*)
10		123.7 (*s*)	10″(14″)	6.63 (*br s*)	108.4 (*d*)
11		155.4 (*s*)	11″(13″)		160.3 (*s*)
12	6.58(*br s*)	103.8(*d*)	12″	6.39(*t* like *m*)	103.2(*d*)
13		160.3 (*s*)			
14	6.62(*br s*)	104.5 (*d*)			
1′		136.5 (*s*)	1‴		133.4 (*s*)
2′(6′)	6.94 (*d*, 8)	129.7 (*d*)	2‴(6‴)	6.94 (*d*, 8)	129.7 (*d*)
3′(5′)	6.66 (*d*, 8)	116.5 (*d*)	3‴(5‴)	6.66 (*d*. 8)	116.3 (*d*)
4′		157.0 (*s*)	4‴		157.2 (*s*)
7′	4.72 (*br s*)	48.8 (*d*)	7‴	3.35 (*d*, 10)	65.8 (*d*)
8′	3.79 (*br d*, 5)	64.5 (*d*)	8‴	3.57 (*t*, 10)	62.2 (*d*)
9′		163.3 (*s*)	9‴		144.9 (*s*)
10′		144.4 (*s*)	10‴(14‴)	6.07 (*m*)^b	107.5 (*d*)
11′		194.1 (*s*)	11‴(13‴)		159.5 (*s*)
12′	3.08 (*d*. 3)	68.7 (*d*)	12‴	6.07 (*m*)^b	102.4 (*d*)
13′		206.0 (*s*)	OHs	7.92 (×2), 8.00,	8.03, 8.12,
14′	3.48 (*br s*)	51.2 (*d*)		8.23 (×2), 8.25	8.80 (each *br s*)

Values are in ppm (δ_H and δ_C). ^{1}H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively. All protons and carbons were assigned by the aid of ^{13}C–^{1}H COSY, COLOC and HMBC spectra. Figures in parentheses are coupling constants (*J*) in Hz.

^{a,b}Overlapping signals.

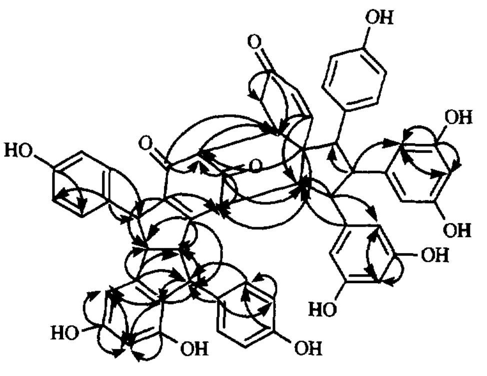
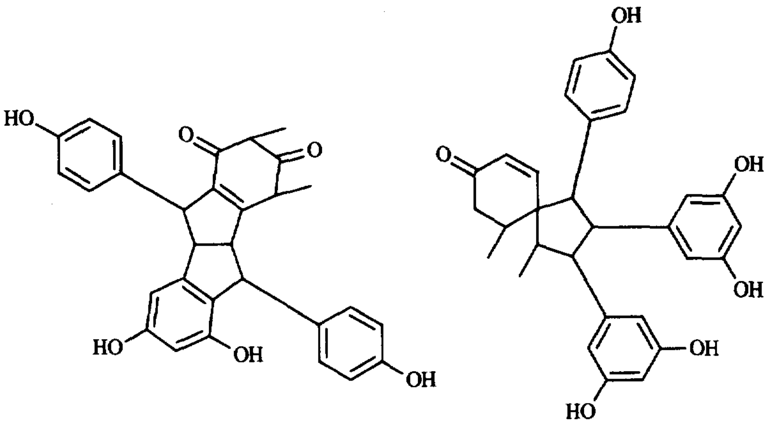


Fig. 1. ^{13}C–^{1}H long-range correlations in COLOC spectrum of **1**.

δ_C 206.0 (C-13′)–δ_H 3.21 (H-7″) and δ_C 68.7 (C-12′)–δ_H 3.27 (H-6″) in the COLOC spectrum showed that **1a** and **1b** were combined in a planar structure.

The relative stereochemistry of leachianol C (**1**) was determined by the results of a phase-sensitive NOESY (PSNOESY) spectrum (Fig. 3) and NOE difference experiments. NOE interactions were observed between H-8/H-8′, H-8/H-2(6), H-8′/H-2′(6′), which indicated that two 4-hydroxyphenyl groups at C-7 and C-7′ were *cis*-oriented towards H-8 and H-8′. On the basis of the following NOE results [H-7/H-3″, H-7′/H-7″, H-2″/H-7″, H-7″/H-10″(14″), H-8″/H-10‴(14‴), H-10″(14″)/H-8‴, H-2‴(6‴)/H-8‴, H-7‴/H-10‴(14‴), H-5″*ax*/H-7‴ and H-12′/H-5″*eq*], the relative configurations were finally concluded as shown in **1**. The presence of a cyclohexenone ring transformed from the 4-hydroxyphenyl group showed that a resveratrol and a pallidol molecule are condensed, respectively, across the locations at C-1″ and C-6″ on the ring. To the best of our knowledge, this resveratrol oligomerization is the first occurrence in nature and characterizes the biosynthetic pathway in the genus *Sophora*.

Leachianol D (**2**), obtained as a brown solid, gave [M – H]$^-$ at *m/z* 679 in the negative ion FAB mass spectrum corresponding to the formula $C_{42}H_{32}O_9$, which indicated that it was a resveratrol trimer. The ^{1}H NMR spectrum (Table 2) showed the presence of (i) six sets of *ortho*-coupled aromatic protons attributable to three 4-hydroxyphenyl groups, (ii) aromatic protons in an AX_2-system due to a 3,5-dihydroxyphenyl group [H-10″(14″)



1a **1b**

Fig. 2. Partial structures of **1**.

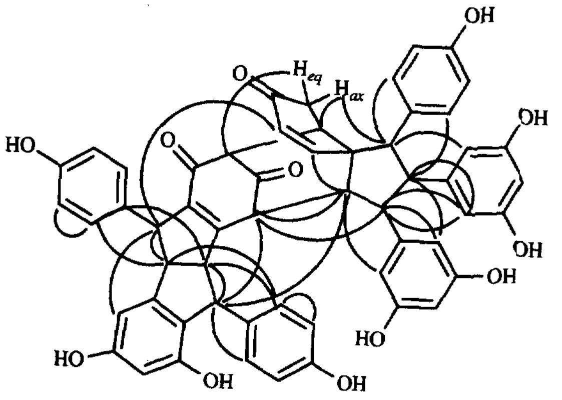


Fig. 3. NOE interactions in PSNOESY spectrum of **1**.

and H-12″], (iii) two aromatic methine protons in a 1,2,3,5-tetrasubstituted benzene (H-12 and H-14), (iv) another aromatic methine proton (H-14′), (v) two sets of mutually coupled aliphatic methine protons (H-8–H-8′ and H-7″–H-8″) and (vi) two aliphatic methine protons (H-7 and H-7′), as well as eight hydroxyl protons. In the ^1H–^1H long range COSY spectrum aliphatic protons at δ_H 3.83 and 3.81 were coupled with benzyl methine protons at δ_H 4.63 and 4.65, respectively, which had further correlations to *ortho*-coupled aromatic protons at δ_H 6.97 and 7.01. In addition, the proton signals at δ_H 3.83 and 3.81 were correlated to those at δ_H 6.64 on the 1,2,3,5-tetrasubstituted benzene and at δ_H 6.73 on a dihydrobenzofuran ring, respectively. In the spectrum, a benzyloxy methine proton at δ_H 5.32 and an adjacent benzyl methine proton at δ_H 4.37 were coupled with aromatic protons at δ_H 7.18 in the 4-hydroxyphenyl group and δ_H 6.12 in the 3,5-dihydroxyphenyl group. The HMBC spectrum (Fig. 4) showed long-range couplings, but no evidence about the location of the dihydrofuran ring or whether the carbon at C-7″ is linked with an oxygen either at C-11′ or at C-13′.

The PSNOESY spectrum (Fig. 5) indicated the planar structure and the relative stereochemistry of leachianol D as follows. With respect to the pallidol moiety, *cis*-orientation among each aryl attached to C-7, C-7′ and H-8, H-8′ was determined by the cross-peaks observed between H-8/H-8′, H-8/H-2(6) and H-8′/H-2′(6′). The correlations between H-7″/H-10″(14″) and H-8″/H-2″(6″) showed the remaining resveratrol molecule to be in a *trans*-configuration. NOE interaction between H-2(6) and H-10″(14″) can be observed when the 4-hydroxyphenyl group at C-7 is situated in a *cis*-orientation towards the 3,5-dihydroxyphenyl group at C-8″. Thus, the structure of leachianol D, including the relative configuration, was established as **2**. Considering the optical parameter in the CD spectrum, leachianol D(**2**) might be an enantiomer of gnetin I [5] obtained from the wood of *Welwitschia mirabilis*, because the Cotton effect reported had the opposite curves to those of **2**. No direct comparison between these two compounds was made. Leachianol E(**3**), obtained as a brown solid, gave a $[M - H]^-$ at m/z 679 in the negative ion FAB mass spectrum and showed similar spectral data to those of leachianol D(**2**), as well as the ^1H and ^{13}C NMR spectra (Table 2). The results of the ^1H–^1H long-range COSY and the HMBC spectrum revealed that the planar structure of **3** is closely related to that of leachianol D(**2**), except for cyclization between C-7″ and the oxygen at either C-11′ or C-13′.

A significant difference between **2** and **3** was the chemical shift values of carbon signals assigned to C-14′, which resonated at δ_C 97.6 in **2**, δ_C 104.7 in **3**. In the case of gnetins C(**6**) [6] and E(**7**) [6, 7], isolated from several *Gnetum* species, the carbon signals at C-10 neighbouring an oxygen in the dihydrofuran ring were observed at δ_C 98.7 and 99.2; those at C-14 vicinal to the hydroxyl group appeared at δ_C 107.3 and 108.1. Since the carbon signals adjacent to the dihydrofuran ring were observed

Table 2. ^{1}H and ^{13}C NMR data of leachianols D(**2**) and E(**3**) in acetone-d_6

	2		**3**			
No.	δ_H	δ_C	δ_H	δ_C	HMBC*	NOE**
1		137.2 (*s*)		137.6 (*s*)		
2(6)	6.97 (*d*, 9)	129.1 (*d*)	7.06 (*d*, 9)	129.3 (*d*)	4	3(5),7,8,8′
3(5)	6.69 (*d*, 9)	115.9 (*d*)	6.76 (*d*, 9)	116.0 (*d*)	1	2(6)
4		156.4 (*s*)		156.6 (*s*)		
7	4.63 (*br s*)	53.4 (*d*)	4.57 (*br s*)	54.9 (*d*)	1,2(6),8′,9′,10′	2(6),8,14
8	3.83 (*brd*, 7)	61.0 (*s*)	3.99(*brd*, 7)	60.4 (*d*)	1,10,9′,10′	2(6),7,2′(6′),8′
9		150.3 (*s*)		150.5 (*s*)		
10		123. (*s*)		123.3 (*s*)		
11		155.3 (*s*)		155.4 (*s*)		
12	6.21 (*br s*)	102.7 (*d*)	6.26 (*br s*)	102.8 (*s*)	10,11,14	
13		159.6 (*s*)[a]		159.6 (*s*)		
14	6.64 (*br s*)	103.3 (*d*)	6.67 (*br s*)	103.5 (*s*)	10,12	7
1′		137.7 (*s*)		137.9 (*s*)		
2′(6′)	7.01 (*d*, 8)	129.1 (*d*)	7.01 (*d*, 8)	129.0 (*d*)	4′	8,3′(5′),7′,8′
3′(5′)	6.71 (*d*, 8)	115.8 (*d*)	6.73 (*d*, 8)	115.9 (*d*)	1′	2′(6′)
4′		156.4 (*s*)		156.4 (*s*)		
7′	4.65 (*br s*)	53.9 (*d*)	4.59 (*br s*)	54.7 (*d*)	8,9,10,1′,2′(6′)	2′(6′),8′,14′
8′	3.81 (*brd*, 7)	60.3 (*d*)	3.95 (*brd*, 7)	61.0 (*d*)	9,10,1′,10′	2(6),8,2′(6′),7′,
9′		150.6 (*s*)		150.3 (*s*)		
10′		124.6 (*s*)		119.3 (*s*)		
11′		159.4 (*s*)[a]		158.2 (*s*)		
12′		115.9 (*s*)		114.6 (*s*)		
13′		162.8 (*s*)		155.6 (*s*)		
14′	6.73 (*br s*)	97.6 (*d*)	6.66 (*br s*)	104.7 (*d*)	10′,12′,13′	7′
1″		133.9 (*s*)		134.4 (*s*)		
2″(6″)	7.18 (*d*, 8)	128.1 (*d*)	6.73 (*d*, 8)	126.9 (*d*)	4″	3″(5″),7″,8″
3″(5″)	6.80 (*d*, 8)	116.1 (*d*)	6.62 (*d*, 8)	115.9 (*d*)	1″	2″(6″),
4″		158.2 (*s*)		157.5 (*s*)		
7″	5.32 (*d*, 6)	94.1 (*d*)	5.34 (*d*, 4)	93.3 (*d*)	11′,12′,2″,6″,9″	2″(6″),8″,10″(14″)
8″	4.37 (*d*, 6)	55.5 (*d*)	4.20 (*d*, 4)	56.8 (*d*)	11′,12′,1″,9″, 10″(14″)	2″(6″),7″ 10″(14″)
9″		146.1 (*s*)		146.5 (*s*)		
10″(14″)	6.12 (*br s*)	106.8 (*d*)	6.14 (*d*, 2)	106.6 (*d*)	12″	7″,8″
11″(13″)		159.6 (*s*)		159.6 (*s*)		
12″	6.17 (*t* like *m*)	102.1 (*d*)	6.18 (*t* like *m*)	101.9 (*d*)	10″,14″	
OH	7.14, 7.81, 8.00(× 2), 8.08(× 3), 8.39 (each *br s*)		7.87, 7.94, 8.07, 8.10 (× 2), 8.16(× 2) 8.27 (each *br s*)			

Values are in ppm (δ_H and δ_C). ^{1}H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively. All protons and carbons were assigned by the aid of ^{13}C–^{1}H COSY, COLOC and HMBC spectra. Figures in parentheses are coupling constants (*J*) in Hz.

*Long-range correlated carbon numbers in HMBC spectrum.

•Proton numbers observed NOE interactions in PSNOESY spectrum.

†Overlapping signals.

at a higher field than those next to the hydroxyl group, the planar structure of **3** was rationalized by leachianol D(**2**).

The relative stereostructure was also explained by the results of the PSNOESY spectrum. The aryl groups at C-7, C-7′ and H-8, H-8′ had a *cis*-orientation as evidenced by the NOE enhancements between H-8/H-8′, H-8/H-2(6) and H-8′/H-2′(6′). The cross-peaks, H-7″/H-10″(14″) and H-8″/H-2″(6″), indicated that the resveratrol molecule was in a *trans*-orientation. Finally, the relative configuration of leachianol E could be shown in **3**. The orientation of the other resveratrol molecule in the pallidol skeleton could not be established at this stage, because the Cotton curves attributed to the locations of C-7″ and C-8″ in the dihydrobenzofuran ring were overlapped with the curves corresponding to the pallidol moiety, though the CD spectrum exhibited similar Cotton effects to those of **2**. In the case of (−)-ε-viniferin [8], curves are observed at 287 (Δε + 1.0) and 238 nm (Δε − 5.9), whereas in pallidol [4] they are at 283 (Δε + 3.9) and 240 nm (Δε − 5.5).

Leachianols F(**4**) and G(**5**) were obtained as a brown solid mixture in a ratio 1:0.8. All signals in the ^{1}H NMR spectrum were assigned by the aid of a ^{1}H–^{1}H long-range

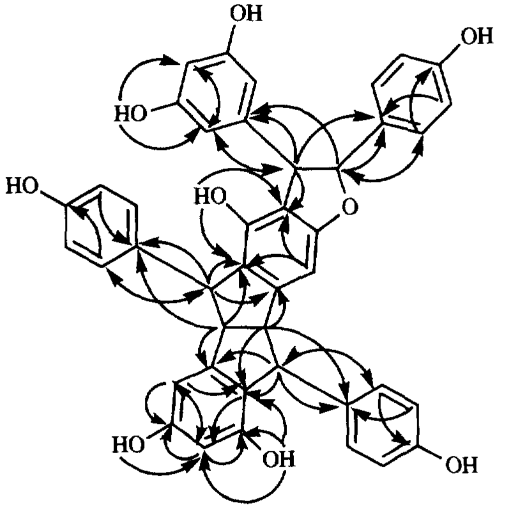


Fig. 4. Long-range correlations in HMBC spectrum of leachianols D (**2**).

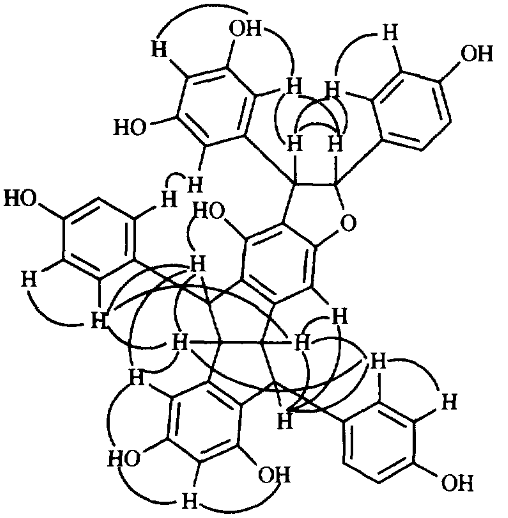
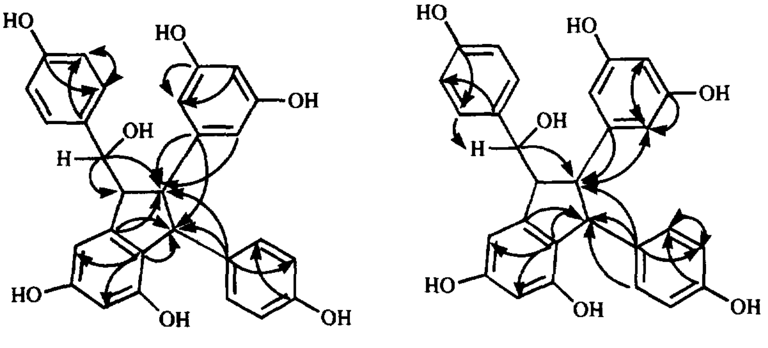


Fig. 5. NOE interactions of leachianols D (**2**) in PSNOESY spectrum.

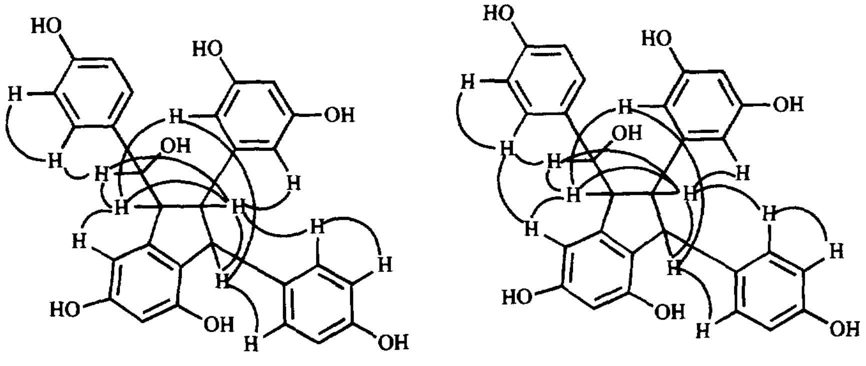
COSY spectrum and exhibited the presence of (i) eight sets of *ortho*-coupled aromatic methine protons derived from four 4-hydroxyphenyl groups, (ii) aromatic protons coupled in an AX_2 system due to two 3,5-dihydroxyphenyl groups, (iii) *meta*-coupled aromatic protons attributable to two 1,2,3,5-tetrasubstituted benzenes (H-12 and H-14), as well as (iv) two sequences of aliphatic methine protons (H-7–H-8 and H-7′–H-8′). In the last methine, a terminal one-proton double-doublet at δ_H 4.47 (**4**: H-7) and 4.47 (**5**: H-7) was coupled with a hydroxyl group at δ_H 4.02 (*d*, $J = 4$ Hz) in **4** and at 4.09 (*d*, $J = 4$ Hz) in **5**, respectively. The COLOC spectrum (Fig. 6) enabled the complete assignments of all ^1H and ^{13}C NMR signals, demonstrating that their planar compositions were identical. In the PSNOESY spectrum (Fig. 7), NOE enhancement between H-8′/H-2′(6′), H-7′/H-10′(14′) and H-8/H-10′(14′) in **4** and **5** indicated that H-8, H-7′ and the aryl at C-8′ were situated in a *cis*-orientation. Proton signals (**4**: δ_H 2.95 and **5**: δ_H 5.75) at relatively higher field required that the aryl at C-7 was located near H-8′ and H-14. These results as well as common coupling constants found in H-7′/H-8′/H-8/H-7/C-7-OH, suggested that the stereostructures of leachianols F and G were as shown in structures **4** and **5**, respectively, which refers only to relative configuration. The planar structures show that **4** and **5** have a common precursor of pallidol and that they are formed through a different biogenetic pathway.

The oligostilbenes obtained from the roots of *S. leachiana* are represented by leachianols A and B [1], and leachianols C–E which are commonly derived from pallidol as precursor. On the contrary, the oligostilbenes in *S. moorcroftiana* are known to contain exclusively miyabenol C [9] and related compounds, which are formed through ε-viniferin. Though these two species show the occurrence of closely similar flavonostilbenes bearing a lavandulyl and/or isoprenyl group [10], the formation of resveratrol oligomers is significantly different. The structures of the oligomers can therefore play an important role, not only in distinguishing between *S. leachiana* and *S. moorcroftiana* but also in expanding the chemosystematics of the genus *Sophora*.



4 **5**

Fig. 6. Long-range correlations in leachianols F (**4**) and G (**5**).



4 **5**

Fig. 7. NOE interactions in leachianols F (**4**) and G (**5**).

Table 3. ^{1}H and ^{13}C NMR data of leachianols F(**4**) and G(**5**) in acetone-d_6

	4		**5**	
No.	δ_H	δ_C	δ_H	δ_C
1		136.0 (*s*)		135.6 (*s*)
2(6)	6.87 (*d*, 8)	128.8 (*d*)	7.07 (*d*, 8)	129.4 (*d*)
3(5)	6.68 (*d*, 8)	115.4 (*d*)	6.72 (*d*, 8)	115.2 (*d*)
4		156.2 (*s*)		157.2 (*s*)
7	4.47 (*dd*, 8, 4)	76.6 (*s*)	4.48 (*dd*, 8, 4)	77.3 (*d*)
8	3.37 (*dd*, 8, 4)	61.7 (*d*)	3.40 (*dd*, 8, 4)	62.5 (*d*)
9		148.6 (*s*)		147.2 (*s*)
10		122.5 (*s*)		123.1 (*s*)
11		155.0 (*s*)[a]		154.8 (*s*)[a]
12	6.30 (*d*, 2)	102.4 (*d*)	6.22 (*d*, 2)	102.4 (*d*)
13		158.7 (*s*)[b]		158.5 (*s*)[b]
14	6.57 (*d*, 2)	106.1 (*d*)	5.75 (*d*, 2)	105.6 (*d*)
1′		137.3 (*s*)		137.9 (*s*)
2′(6′)	6.85 (*d*, 8)	129.2 (*d*)	6.87 (*d*, 8)	129.2 (*d*)
3′(5′)	6.73 (*d*, 8)	115.6 (*d*)	6.71 (*d*, 8)	115.6 (*d*)
4′		156.3 (*s*)		157.1 (*s*)
7′	4.23 (*d*, 4)	55.5 (*d*)	4.26 (*d*, 4)	55.9 (*d*)
8′	2.95 (*t*, 4)	59.4 (*d*)	3.48 (*t*, 4)	59.0 (*d*)
9′		150.5 (*s*)		151.3 (*s*)
10′(14′)	5.92 (*d*. 2)	106.0 (*d*)	6.14 (*d*, 2)	106.2 (*d*)
11′(13′)		159.1 (*s*)		159.2 (*s*)
12′	6.12 (*t*, 2)	101.2 (*d*)	6.16 (*t*, 2)	101.0 (*d*)
7-OH	4.02 (*d*, 4)		4.09 (*d*, 4)	

Footnotes as for Table 1.

EXPERIMENTAL

Plant material and extraction. As described in our previous paper [1].

Isolation of compounds. The EtOAc-soluble layer of an Me_2CO extract of roots [1] was purified by silica gel CC with a benzene–acetone system to give 5 frs. Frs 4–5 containing **1**–**5** were subjected to repeated vacuum liquid chromatography on silica gel 60H (Merck) eluting with $CHCl_3$–MeOH (10:1) and Sephadex LH-20 CC eluting with MeOH or Me_2CO–H_2O (4:1), to give **1** (56 mg), **2** (30 mg), **3** (54 mg) and a mixt. of **4** and **5** (205 mg).

Leachianol C (**1**). Brown solid. Negative ion FABMS m/z 907 $[M - H]^-$. UV (nm, MeOH): 212, 220sh, 270. $[\alpha]_D^{24}$ − 30.3° (MeOH; *c* 0.10). CD (MeOH, nm): $\Delta\varepsilon_{250}$ + 5.5, $\Delta\varepsilon_{283}$ − 6.6, $\Delta\varepsilon_{298}$ − 5.0, $\Delta\varepsilon_{340}$ + 2.8. IR (KBr, cm^{-1}): 3400, 1720, 1670, 1610, 1520. ^{1}H and ^{13}C NMR: Table 1.

Leachianol D (**2**). Brown solid. Negative ion FABMS m/z 679 $[M - H]^-$. UV (MeOH, nm): 206, 219sh, 285.

$[\alpha]_D^{25}$ − 18.7° (MeOH; *c* 0.11). CD (MeOH, nm): $\Delta\varepsilon_{240}$ − 10.1, $\Delta\varepsilon_{270}$ − 1.5, $\Delta\varepsilon_{285}$ + 3.0, $\Delta\varepsilon_{298}$ − 1.3. IR (KBr, cm^{-1}): 3400, 1640, 1600. ^1H and ^{13}C NMR: Table 2.

Leachianol E (**3**). Brown solid. Negative ion FABMS *m/z* 679 $[M - H]^-$. UV (MeOH, nm): 210, 217sh, 280. $[\alpha]_D^{26}$ − 84.8° (MeOH; *c* 0.12). CD (MeOH, nm): $\Delta\varepsilon_{242}$ − 8.1, $\Delta\varepsilon_{270}$ − 1.2, $\Delta\varepsilon_{285}$ + 3.1. IR (KBr, cm^{-1}): 3300, 1630, 1600. ^1H and ^{13}C NMR: Table 2.

Mixture of leachianols F (**4**) *and G* (**5**). Brown solid. Negative ion FABMS *m/z* 481 $[M - H]^-$. UV (MeOH, nm): 218, 280. $[\alpha]_D^{24}$ 5.9° (MeOH; *c* 0.10) IR (KBr, cm^{-1}): 3330, 1610, 1520 ^1H and ^{13}C NMR: Table 3.

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