Phytochemistry, Vol. 31, No. 2, pp. 633–638, 1992
Printed in Great Britain.

0031-9422/92 $5.00 + 0.00
Pergamon Press plc

A DIMERIC STILBENE FROM *GNETUM PARVIFOLIUM*

M. LIN,* J. B. LI, S. Z. LI, D. Q. YU and X. T. LIANG

Institute of Materia Medica, Chinese Academy of Medical Sciences, 1 Xian Nong Tan Street, Beijing 100050, People's Republic of China

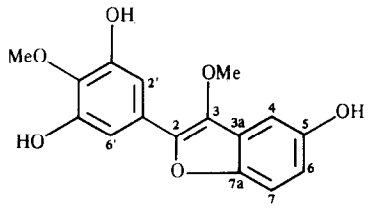
(*Received in revised form* 29 *May* 1991)

Key Word Index—*Gnetum parvifolium*; Gnetaceae; lianas; stilbenes; 3′,5,7-trihydroxy-3-methoxyflavone; isorhapotigenin-12-*O*-D-glucopyranoside; gnetifolin C, D.

Abstract—Ten constituents have been isolated from lianas of *Gnetum parvifolium*. Two novel dimeric stilbenes, gnetifolin C and D, a new stilbene glucoside and flavone, gnetifolin E and B have been identified along with six known compounds. Their structures were deduced on the basis of spectroscopic evidence.

INTRODUCTION

Gnetum parvifolium grows in the southern part of China and has been used in the treatment of bronchitis and arthritis in folk medicine. Previously six components: gnetifolins A (**11**) and C, resveratol (**4**), isorhapotigenin (**5**), β-sitosterol [1] and higenamine [2], were isolated from the lianas of *G. parvifolium*. The structure of gnetifolin C was not assigned due to the scarcity of material. In a further study, gnetifolin C and nine other compounds were isolated from the ethyl acetate-soluble fraction of an aqueous ethanolic extract. Two of the four new structures were determined as dimeric stilbenes named gnetifolins C (**1**) and D (**2**) mainly by the use of 2D NMR techniques (500, 600 MHz). Their structures are different from other bicyclo octanoid and hydrobenzofuranoid stilbenes obtained from *Gnetum* species [3]. The structure of the new components, gnetifolins B and E, were established as 3′,5,7-trihydroxy-3-methoxyflavone and isorhapotigenin-12-*O*-D-glucopyranoside, respectively, the six known compounds as syringic acid [4], pinosylvin [4], isorhapotigenin-3-*O*-D-glucopyranoside [5], *p*-hydroxybenzoic acid [4], gnetol [6] and ε-viniferin [3].



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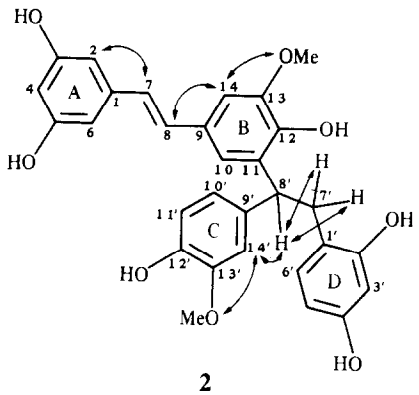

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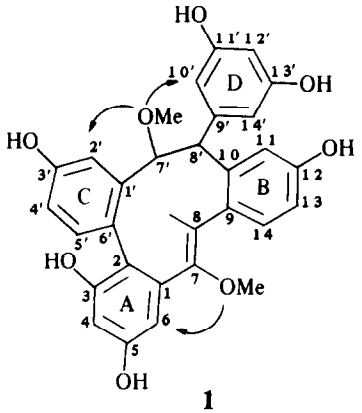
RESULTS AND DISCUSSION

Gnetifolin C (**1**), an amorphous powder, had a molecular formula $C_{30}H_{26}O_8$. FD mass spectrometry and ^{1}H NMR of its acetyl derivative suggested the presence of six hydroxyl groups in the molecule. The UV absorptions of **1** indicated that it is a hydroxystilbene derivative; no shift was observed with added sodium acetate–boric acid, indicating the absence of *ortho*-dihydroxyl groups in the molecule. The IR spectrum showed the presence of hydroxyl groups, aromatic and olefinic groups, but no carbonyl group. The ^{1}H NMR spectrum of **1** displayed the following features (Table 1): 12 aromatic and olefinic protons at δ7.06–6.02, two methine groups at δ4.27 (1H, *s*, H-8′), 4.19 (1H, *s*, H-7′) and two methoxyl groups at δ3.71 (3H, *s*), 3.57 (3H, *s*) and six hydroxyl groups in the region δ7.17–8.09. The ^{1}H–^{1}H COSY (600 MHz DQPH) spectrum showed 11 aromatic protons to be located on four aromatic rings. Two signals of protons H-6 and H-4 were attributed to *meta* coupling ($J = 2$ Hz) on ring A. The signals of H-11, H-13, H-14 and H-2′, H-4′, H-5′, belonged to ABX systems ($J = 8$, 2 Hz) on rings B and C, respectively. Protons H-12′, H-10′ and H-14′ were attributed to an AB_2 system ($J = 2$ Hz) on ring D. The signal of H-8 without coupling was assigned to an ethylenic chain. The signal at δ8.90 was attributed to two symmetric hydroxyl groups on ring D. The remaining four signals of hydroxyl groups at δ7.17, 7.44, 7.60 and 8.17 were located on rings A–C. The ^{13}C NMR (150 MHz)

*Author to whom correspondence should be addressed.

Table 1. ^{1}H, ^{13}C NMR and long-range ^{13}C–^{1}H NMR data of compound **1** [$(CD_3)_2CO$, 600 MHz]

H		C		Cross peaks to protons
		1	147.31	H-8
		2	130.22	H-5′
		3	155.93	H-4
4	6.30 *d* (2)	4	103.87	
		5	159.71	H-4
6	6.78 *d* (2)	6	98.45	
8	7.06 *s*	7	148.09	MeO, H-8
		8	123.26	
		9	138.43	H-8′, H-14
		10	145.81	H-11
11	6.74 *d* (2)	11	111.76	H-8′
		12	148.03	
13	6.50 *dd* (8, 2)	13	120.08	H-14
14	6.64 *d* (8)	14	115.56	
		1′	146.64	H-2′
2′	6.88 *d* (2)	2′	112.22	
		3′	149.13	
4′	6.83 *dd* (8, 2)	4′	123.85	H-5′
5′	6.68 *d* (8)	5′	115.58	H-4′
		6′	142.86	H-4′, H-7′
7′	4.19 *s*	7′	57.92	
8′	4.27 *s*	8′	60.70	H-10′, H-14′
		9′	124.58	H-7′, H-8′, H-10′, H-14′
10′, 14′	6.34 *d* (2)	10′, 14′	106.34	H-8′
		11′, 13′	159.83	H-12′, H-10′, 14′
12′	6.20 *t* (2)	12′	101.57	
MeO	3.71 *s*	MeO	56.22	
MeO	3.57 *s*	MeO	56.12	
OH	7.17			
	7.44			
	7.60			
	8.17			
	8.90 × 2			



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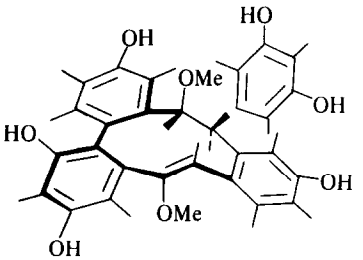


1a

spectrum of **1** displayed 28 signals representing 30 carbons. The ^{13}C–^{1}H COSY spectrum indicated the presence of 14 aromatic quaternary carbon signals at δ159.83–124.58, 12 protonated aromatic carbons signals at δ123.85–98.45, two methine carbons at δ60.70 (C-8′), δ57.92 (C-7′) and two methoxyl at δ56.22, 56.12. The locations of the two methoxyl groups (δ3.57, 3.71) were at positions C-7′ and C-7, respectively, which were supported by NOE measurements. The signals of H-2′ (δ6.88), H-10′ (and H-14′, δ6.34) and H-6 (δ6.78) were enhanced by 5.1, 2.1 and 5.45% after irradiation of the signals of methoxyl groups at δ3.57 and 3.71, respectively. The former was arbitrarily assigned the α-configuration and the latter should be *trans*-oriented to the H-8. The vicinal coupling constant between H-7′ and H-8′ was *ca* zero corresponding to a vicinal dihedral angle of *ca* 90°,

signifying that the vicinal protons should be *cis*-oriented. The structure **1** was supported further by long-range ^{13}C–^{1}H shift correlation (COLOC) for connectivities of two and three bonds (7–10 Hz) [7]. Nine signals of cross peaks were quite useful for elucidation of the structure, especially for the arrangement of the four aromatic rings (Table 1). The quaternary carbons at δ147.31 (C-1), 138.43 (C-9), 130.22 (C-2), 142.86 (C-6′) and 124.58 (C-9′) correlated with H-8; H-8′, H-14′; H-5′; H-4′, H-7′, and H-7′, H-8′, H-10′ (and H-14′), respectively. The aromatic carbons (C-11) at δ111.78 and (C-10′ or C-14′) 106.34 showed a long-range coupling with H-8′. The olefinic carbon at δ148.09 (C-7) and the methine group at δ60.70 were correlated with the protons of the methoxyl group at δ3.71 and the aromatic protons H-10′ and H-14′, respectively.

From analysis of the spectral data of **1**, it proved possible, to assign unambiguously all of the ^{1}H and ^{13}C NMR signals; thus, its stereochemical structure is as shown in **1a**.

The UV spectrum of gnetifolin D (**2**), a yellowish amorphous powder, indicated the characteristics of a stilbene skeleton with hydroxyl groups which again showed no shift after addition of sodium acetate–boric acid, suggesting the absence of *ortho* dihydroxy groups in the molecule. The IR spectrum showed hydroxyl groups (3400 cm^{-1}), olefinic and aromatic groups (1600, 1510 cm^{-1}) with no carbonyl group. The FD mass spectrum of **2** showed a $[M]^+$ at *m/z* 516 corresponding to $C_{30}H_{28}O_8$ and three fragment peaks at *m/z* 492, 259 and 258. The ^{1}H NMR of gnetifolin D displayed 11 aromatic and two olefinic protons at δ7.17–6.05. The signals at δ3.47 (1H, *dd*, J = 13, 7.8 Hz, H-7′a) and 3.37 (1H, *dd*, J = 13, 7.8 Hz, H-7′b) were due to the two protons of the methylene group. The methine proton at δ4.88 (1H, *dd*, J = 7.8, 7.8 Hz, H-8′) was evidently vicinal to the methylene group on the basis of the coupling constants. The ^{1}H–^{1}H COSY spectrum showed aromatic protons located on four (A–D) rings. Two protons, H-10 and H-14 with *meta* coupling (J = 2 Hz) are placed on ring B and protons H-10′, H-11′, H-14′, and H-3′, H-6′, H-5′ are two sets of ABX systems located on aromatic rings C and D respectively. Protons H-2, H-4, H-6 belong to an AB_2 system (J = 2 Hz) on ring A. The ^{13}C NMR spectrum of **2** showed 25 signals representing 30 carbons. The ^{13}C–^{1}H COSY spectrum showed the existence of 13 aromatic quaternary carbons in the range of δ158.8–137.4 (Table 2), 11 unsubstituted aromatic and two olefinic carbons, one methylene and one methine group at δ130.5–100.8, 40.0 and 42.4, respectively. The remaining two signals at δ56.2 and 56.3 were two methoxyl groups. According to this spectral data, structure **2**

Table 2. ^{1}H, ^{13}C NMR and ^{13}C–^{1}H NMR long-range spectral data of compound **2** [$(CD_3)_2CO$, 500 MHz]

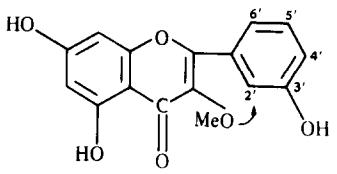
H		C		Cross peaks to protons
		1	137.36	
2, 6	6.23 *d* (2)	2, 6	108.31	H-4
		3,5	158.74	
4	6.06 *t* (2)	4	100.81	H-2, H-6
7	6.85 *d* (16)	7	126.93	H-8
8	6.87 *d* (16)	8	128.54	H-10, H-14
		9	137.71	
10	6.52 *d* (2)	10	106.27	
		11	130.52	H-10′, H-14′*
		12	157.20	
		13	148.54	H-14, MeO
14	7.15 *d* (2)	14	110.96	H-8
		1′	145.43	H-5′
		2′	157.20	
3′	6.52 *d* (2)	3′	106.27	H-5′
		4′	157.20	
5′	6.92 *dd* (8, 2)	5′	120.95	
6′	6.62 *d* (8)	6′	114.84	
7′a	3.47 *dd* (13, 7.8)	7′	40.00	
7′b	3.37 *dd* (13, 7.8)			
8′	4.88 *dd* (7.8, 7.8)	8′	42.40	
		9′	145.03	H-14′
10′	6.92 *dd* (2)	10′	121.32	H-11′
11′	6.75 *d* (8)	11′	115.37	H-10′, H-14′
		12′	147.32	H-11′, H-14′
		13′	147.45	H-14′, MeO
14′	7.17 *d* (2)	14′	113.86	H-10′
MeO	3.74	MeO	56.16	
MeO	3.85	MeO	56.25	

*Cross peaks of 4-bonds could sometimes be observed in the COLOC spectrum.

was deduced to be a dimeric stilbene derivative. The arrangement of the four rings and the location of substituted groups were established by COLOC and NOE difference spectra (Table 2, and in formula **2**). Thus, the structure of gnetifolin **D** was assigned as **2**.

The IR spectrum of gnetifolin E (**7**) showed hydroxyl (3700 cm^{-1}) and aromatic (1600, 1500 cm^{-1}) groups, while the UV spectrum was similar to compound **5** [1]. The mass spectrum FAB showed *m/z* 421 $[M+1]^+$ and 259 [aglycone $+1]^+$. The EI mass spectrum of the acetyl derivative displayed *m/z* 672 $[M]^+$, indicating the presence of six acylated hydroxyl groups. Therefore, the molecular formula of **7** was deduced as $C_{21}H_{24}O_9$. The ^1H NMR spectrum of **7** was similar to that of **5** [1] showing the presence of a methoxy group and a *trans* olefinic group and two aromatic rings with 1,3,4(catechol-type) and 1,3,5(resorcinol-type)-trisubstitution. By comparison of ^1H and ^{13}C NMR spectral data with **8** [5], one β-glucosidic unit should be attached to the catechol-type ring (C-12). The location of methoxy group was established by NOE experiments. The aglycone and the sugar were confirmed to be isorhapontigenin and D-glucose, respectively, by acid hydrolysis. From these chemical and spectroscopic data, **7** was characterized as isorhapontigenin-12-*O*-D-glucopyranoside.

Gnetifolin **B** (**3**), yellow crystals, molecular formula $C_{16}H_{12}O_6$, exhibited IR absorption bands for hydroxyl (3310 cm^{-1}), aromatic ring (1610, 1500 cm^{-1}) and chelated carbonyl group (1640 cm^{-1}). The UV spectrum showed absorption maxima at 245 (sh), 268 and 345 nm. Diagnostic reagents (NaOMe, $AlCl_3$, $AlCl_3$–HCl, NaOAc) for UV spectra resulted in bathochromic shifts suggesting a 5,7,3-trihydroxyl, no 3,4′ hydroxyl groups flavone system. The ^1H NMR spectrum supported these conclusions. The signals exhibited at δ6.54 and 6.20 for H-8 and H-6 as *meta* coupled aromatic protons. For **B** ring, two multiplets at δ7.57 (2H, *m*) and 6.93 (2H, *m*) can be assigned to H-2′, H-5′ and H-4′, H-6′ respectively. The methoxy signal at δ3.95 assigned to the 3-position was established by a NOE experiment. The proton H-2 was enhanced by 2.7%, but the remaining signals on the **B** ring were not affected. Exchangeable signals at δ12.97, 10.82 and 9.97 were ascribed to hydroxyl groups at the 5,7 and 3′ positions, respectively. Thus, **3** is 5,7,3′-trihydroxy-3-methoxy-flavone.



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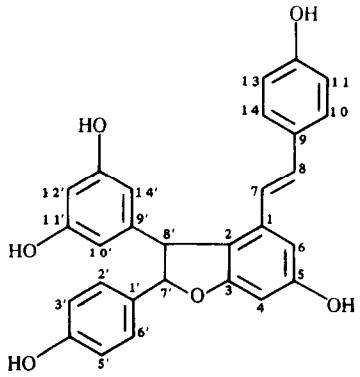

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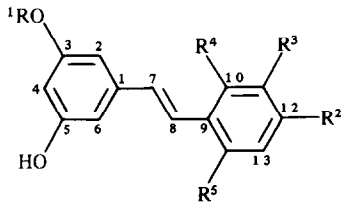

	R^1	R^2	R^3	R^4	R^5	
4	H	OH	H	H	H	Resveratral
5	H	OH	OMe	H	H	Isorhapotigenin
6	H	H	H	H	H	Pinosylvine
7	H	OGlc	OMe	H	H	Genetifolin E
8	Glc	OH	OMe	H	H	Isorhapotigenin-3-*O*-D-glucopyranoside
9	H	H	H	OH	OH	Gnetol

EXPERIMENTAL

Mps: uncorr. IR spectra were recorded in KBr pellets. ^1H NMR, ^{13}C NMR and 2D NMR were determined using TMS as int. ref. Low pressure CC and reverse-phase chomatography were performed on silica gel (10–14 μm) and Lobar RP-8 (Merck) (40–63 μm).

Plant material. Lianas of *G. parvifolium* (Warb.) C. Y. Cheng were collected from Guangxi province of China in the spring and identified by Professor W. Z. Song of our Institute.

Extraction and isolation. Powdered lianas (30 kg) were extracted with 60% EtOH. The extract was concd to yield 2.35 kg of gum which was divided into Me_2CO sol. and insol. frs. The Me_2CO -sol. fr. was further divided into EtOAc sol. and insol. frs. The concd EtOAc-sol. fr. was chromatographed on a silica column (1.5 kg) with $CHCl_3$–EtOAc collecting 175 frs (500 ml each) and combining to give frs 1–5. Fr. 1 (115 g) was purified by silica gel CC using $CHCl_3$–MeOH (19:1), hexane–Me_2CO (3:2) and $CHCl_3$–MeOH (97:3) successively to obtain syringic acid and β-sitosterol. Fr. 2 (95 g) was rechromatographed on a silica column with $CHCl_3$–EtOAc in different ratios giving frs I–VIII. Fr. II was further purified on silica gel (low pressure column) and on a RP-8 column yielding **6** and **3**. Fr. III consisted mainly of **5**. Fr. IV was rechromatographed on a RP-8 column with MeOH–H_2O (11:9) and further purified by prep. TLC giving **2**. Fr. V consisted mainly of **4**. Frs VI–VII were rechromatographed on silica gel with $CHCl_3$–MeOH (19:1) and petrol–EtOAc (1:1) to furnish *p*-hydroxybenzoic acid. Fr. 3 (135 g) was fractionated

Table 3. ^1H and ^{13}C NMR spectral data of compounds **7** and **8** [$(CD_3)_2CO$, 500 MHz]

H	7	8	C	7	8
2 }	6.49 *d* (2H, 2)	6.67 *s* (1H)	1	140.708	140.427
6 }		6.79 *s* (1H)	2 }	105.741	108.064
4	6.22 *t* (1H, 2)	6.50 *t* (1H, 2)	6 }		106.165
10	7.20 *d* (1H, 2)	7.21 *d* (1H, 1.8)	3 }	159.505	159.375
13	6.98 *d* (1H, 9)	6.95 *d* (1H, 8)	5 }		160.165
14	7.08 *dd* (1H, 9, 2)	7.02 *dd* (1H, 8, 1.8)	4	102.602	103.774
7	6.92 *d* (1H, 16)	6.95 *d* (1H, 16)	9	133.190	130.292
8	6.99 *d* (1H, 16)	7.08 *d* (1H, 16)	10	120.665	121.207
OMe	3.84 *s* (3H)	3.89 *s* (3H)	13	117.564	115.692
Glucose 1′	4.89 *d* (1H, 7)	4.93 *d* (1H, 7.6)	12	147.560	147.556
2′–6′	3.84–3.32 (7H)	3.10 3.93 (7H)	11	150.607	148.553
			14	111.038	110.275
			7	128.464	126.646
			8	128.781	129.866
			OME	56.426	56.237
			Glucose 1′	102.323	101.989
			2′	74.478	74.512
			3′	77.777	77.611
			4′	71.255	71.080
			5′	77.565	77.702
			6′	62.450	62.564

by silica gel CC with $CHCl_3$–MeOH (9:1) and further purification on several RP-8 columns to obtain **9**, **10**, **1**, **7** and **8**.

Gnetifolin B (**3**). Yellow crystals, mp 325–328°. HRMS: Found: $[M]^+$ 300.0632, $C_{16}H_{12}O_6$ requires 300.0630. UV λ_{max}^{MeOH} nm: 245, 268, 345; (MeOH + NaOMe) 263, 403; (MeOH + $AlCl_3$) 260, 275, 355, 388; (MeOH + $AlCl_3$ + HCl) 260, 276, 352, 385; (MeOH + NaOAc) 263, 315 (sh), 399. EIMS *m/z* (rel. int.): 300 $[M]^+$ (100), 285 (0.01), 257 (10), 229 (10), 148 (18), 136 (10). IR ν_{max}^{KBr} cm^{-1}: 3200, 1640, 1610, 1590, 1550, 1490. ^1H NMR (400 MHz, DMSO-d_6): δ 7.57 (2H, *m*, H-5′, H-2′), 6.93 (2H, *m*, H-6′, H-4′), 6.54 (1H, *d*, *J* = 2 Hz, H-8), 6.20 (1H, *d*, *J* = 2 Hz, H-6), 3.95 (3H, *s*, OMe).

Gnetifolin C (**1**). Amorphous powder. UV λ_{max}^{EtOH} nm (log ε): 283 (3.98), 303 (4.15), 323 (4.17), 336 (4.06). IR ν_{max}^{KBr} cm^{-1}: 3380, 1600, 1510, 1450. $[\alpha]_D^{14}$ 0° (EtOH). CD (MeOH; *c* 0.34 mg/ml) [θ]: −29 632 (225), +74 580 (240). FDMS *m/z* (rel. int.): 514 $[M]^+$ (40), 513 $[M+1]^+$ (100), 391 (70), 390 (60), 377 (40), 359 (10), 137 (30), 109 (18). Found: C, 64.65, H, 5.04, $C_{30}H_{26}O_8$ 2.5 H_2O requires: C, 64.40, H, 5.54%. ^1H NMR, ^{13}C NMR and COLOC see Table 1. *Acetylation of compound* **1**. Compound **1** (20 mg) was acetylated with Ac_2O–pyridine by the usual method to give crude acetyl compound. Purification by prep. TLC ($CHCl_3$–Me_2CO, 99:1) afforded 17 mg crystals, mp 154–158°. FDMS *m/z* 766 $[M]^+$. Found: C, 64.16, H, 4.91, $C_{30}H_{26}O_8$ $(MeCO)_6 \cdot H_2O$. requires: C, 64.28, H, 5.68%. IR ν_{max}^{KBr} cm^{-1}: 1762. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (1H, *s*, H-6), 7.47 (1H, *d*, *J* = 2 Hz, H-2′), 6.98 (1H, *dd*, *J* = 8, 2 Hz, H-4′), 6.94 (1H, *d*, *J* = 2 Hz, H-6), 6.93 (1H, *d*, *J* = 2 Hz, H-11), 6.92 (1H, *d*, *J* = 8 Hz, H-5′), 6.91 (1H, *d*, *J* = 8 Hz, 14-H), 6.90 (2H, *d*, *J* = 2 Hz, H-10′, 14′), 6.90 (1H, *d*, *J* = 2 Hz, H-4), 6.85 (1H, *t*, *J* = 2 Hz, H-12′), 6.60 (1H, *dd*, *J* = 8, 2 Hz, H-13), 4.64 (1H, *s*, H-8′), 4.39 (1H, *s*, H-7′), 3.73 (3H, *s*, OMe), 3.49 (3H, *s*, OMe), 2.31, 2.22, 2.18, 1.92 (6 × Ac).

Gnetifolin D (**2**). Yellowish amorphous solid. $[\alpha]_D^{28}$ +0.14° (MeOH; *c* 0.007). UV λ_{max}^{MeOH} nm (log ε): 223 (4.58), 285 (4.23), 305 (4.34), 330 (4.48), 345 (4.28). FDMS *m/z* (rel. int.):516 ($[M]^+$, 100), 498 (22), 259 (14), 258 (4). IR ν_{max}^{KBr} cm^{-1}: 3400, 1600, 1510. ^1H, ^{13}C NMR, COLOC see Table 2. The observed difference NOEs are summarized in structure **2**. Acetyl derivative of compound **2**. Crystals, mp 94–96°. EIMS *m/z* (rel. int.): 768 ($[M]^+$, 3), 726 (13), 684 (1), 600 (0.7), 558 (0.8), 384 (3), 342 (36), 300 (35), 258 (58). ^1H NMR (90 MHz, $CDCl_3$): δ 2.00, 2.19, 2.04, 2.08 (18 H, 4*s*, Ac), 3.62 (3H, *s*, OMe), 3.81 (3H, *s*, OMe), 6.52–6.96 (12H, *m*, aromatic and olefinic-H), 4.40 (1H, *dd*, *J* = 7.8, 7.8 Hz, H-8′), 3.50 (1H, *dd*, *J* = 13, 7.8, H-7′), 3.30 (1H, *dd*, *J* = 13, 7.8, H-7′).

Gnetifolin E (**7**). Off-white crystals, mp 140–43°. $[\alpha]_D^{15}$ −30.3° (Me_2CO; *c* 0.98). UV λ_{max}^{MeOH} nm (log ε): 218 (4.42), 235 (4.30), 302 (4.42), 395 (4.50). IR ν_{max}^{KBr} cm^{-1}: 3499, 1600, 1500. FAB-MS: *m/z* (rel. int.): 421 $[M+1]^+$ (10), 259 ([aglycone + 1]$^+$, 100). Found C, 55.55, H, 5.91, $C_{21}H_{24}O_9 \cdot 2H_2O$ requires C, 55.26, H, 6.14. ^1H NMR, ^{13}C NMR see Table 3. NOE enhancement of H-10 was 8.4% on irradation of the OMe group. *Hydrolysis of compound* 7. Compound 7 (5 mg) was dissolved in 2 ml Me_2CO–H_2O (1:1), 1 ml of 5% H_2SO_4 was added and the mixt. refluxed for 4 hr. The reaction mixt. was diluted with H_2O and extracted with EtOAc. The EtOAc layer gave isorhapotigenin which was identified by TLC comparison with an authentic sample. A sample of **7** was applied to a TLC plate, placed in a container filled with HCl gas and heated for 8 hr at 60°. The plate was then developed with *n*-BuOH–HOAc–H_2O (4:1:5) to give a spot of R_f 0.49, the same as that of glucose. Acetyl derivative of gnetifolin E, crystals, mp 147–150°. EIMS *m/z* (rel. int.): 672 $[M]^+$ (0.3), 342 (10), 331 (11), 271 (5), 258 (9), 229 (3), 211 (5), 169 (86), 109 (52).

Pinosylvin (**6**). Needles, mp 153–155°. UV λ_{max}^{MeOH} nm: 210, 215 (sh), 227, 298, 308. IR ν_{max}^{KBr} cm^{-1}: 1620, 1590, 1580. ^1H NMR [90 MHz, $(CD_3)_2CO$]: δ 6.24 (1H, *t*, *J* = 2 Hz, H-4), 6.46 (2H, *d*, *J* = 2 Hz, H-2, H-6), 7.03 (2H, *s*, H-7, H-8), 7.30 (5H, *m*, aromatic-H). Acetyl derivative: EIMS *m/z* (rel. int.): 296 $[M]^+$ (40), 254 $[M-42]^+$ (25), 212 $[M-2\times42]^+$ (100).

Isorhapotigenin-3-O-D-glucopyranoside (**8**). Yellowish amorphous powder. $[\alpha]_D^{25}$ −46.3° (Me_2CO, *c* 0.52). UV λ_{max}^{MeOH} (log ε): 202 (4.47), 218 (4.44), 302 (4.30) (4.38). FABMS *m/z* (rel. int.): 421 $[M+1]^+$, (15), 259 ([aglycone + 1]$^+$, 55). ^1H NMR, ^{13}C-NMR see Table 3. The signal of H-10 was enhanced 8.4% after irradation of the OMe group.

ε-Viniferin (**10**). Amorphous powder. EIMS *m/z* (rel. int.): 454 $[M]^+$ (100). IR ν_{max}^{KBr} cm^{-1}: 3380, 1600, 1510. UV λ_{max}^{MeOH} nm (log ε): 225 (4.65), 286 (4.28), 3.08 (4.44), 324 (4.52). ^1H NMR

(500 MHz, $(CD_3)_2CO$]: δ 7.16 (2H, *dd*, $J = 8.6$, 2 Hz, H-10, H-14), 6.74 (2H, *dd*, $J = 8.6$, 2 Hz, H-11, H-13), 6.89 (1H, *d*, $J = 16$ Hz, H-7), 6.69 (1H, *d*, $J = 16$ Hz, H-8), 6.32 (1H, *d*, $J = 2$ Hz, H-4), 6.7 (1H, *d*, $J = 2$ Hz, H-6), 7.19 (2H, *dd*, $J = 8.5$, 2 Hz, H-2′, H-6′), 6.83 (2H, *dd*, $J = 8.5$, 2 Hz, H-3′, H-5′), 5.42 (1H, *d*, $J = 5.5$ Hz, H-7′), 4.45 (1H, *d*, $J = 5.5$ Hz, H-8′), 6.25, 6.24 (3H, overlaping peaks, H-10′, H-12′, H-14′). ^{13}C NMR [125 MHz, $(CD_3)_2$ CO]: 129.8 (C-9), 128.6 (C-10), C-14), 116.2 (C-11, C-13), 158.2 (C-12), 123.5 (C-8), 130.1 (C-8), 136.4 (C-1), 119.7 (C-2), 162.4 (C-3), 96.7 (C-4), 159.5 (C-5), 104.2 (C-6), 133.8 (C-1′), 127.8 (C-2′, C-6′), 116.1 (C-3′, C-5′), 158.2 (C-4′), 93.9 (C-7′), 57.2 (C-8′), 147.3 (C-9′), 102.0 (C-12′), 106.9 (C-10′, C-14′), 159.6 (C-11′, C-13′) [4]. Spectral data were supported by ^{1}H–^{1}H COSY and COLOC.

Acknowledgements—We thank Dr D. Moskan of Bruker Analytical and Medical Instruments Laboratory for measurement of ^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H COSY DQPH, ^{13}C–^{1}H COSY and COLOC (600 MHz) spectra. Some of the ^{1}H NMR (400 MHz) spectra were measured at the Academy of Military Medical Science. Other spectra were measured by the Department of Instrumental Analysis of our institute.

REFERENCES

1. Li, J. B., Lin, M., Li, S. Z. and Song, W. Z. (1991) *Acta. Pharm. Sinica* **26**, 437.
2. Fujian Institute of Medica and Medicina. (1980) *Acta. Pharm. Sinica.* **15**, 434.
3. Lins, A. P., Nilce, M., Ribeiro, S., Gottlieb, O. R. and Gottlieb, H. E. (1982) *J. Nat. Prod.* **45**, 754.
4. Windholz, M. (1976) *Merck Index*, 9th Edn.
5. Andrews, D. H., Hoffman, J. C., Purves, C. B., Quon, H. H. and Swan, E. P. (1968) *Can. J. Chem.* **46**, 2525.
6. Zaman, A., Prakash, S. and Wizarat, K. (1983) *Indian. J. Chem.* **22B**, 101.
7. Summers, M. F., Marzill, U. G. and Bax, A. (1986) *J. Am. Chem. Soc.* **108**, 4285.