Antifungal Stilbenoids from *Stemona collinsae*

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Fifteen new stilbenoids including 11 phenylbenzofurans, the stemofurans A−K (**1**−**11**), and four dihydrostilbenes, the stilbostemins A (**15**), C (**17**), E (**19**), and F (**20**), were isolated and identified from a methanolic extract of *Stemona collinsae* roots together with five known derivatives, the stilbenes pinosylvin (**13**) and 4′-methylpinosylvin (**14**), the dihydrostilbenes, stilbostemins B (**16**) and D (**18**), and the dihydrophenanthrene racemosol (**12**) as well as (+)-sesamin, coniferyl alcohol, and stigmasterol. Bioautographic tests with *Cladosporium herbarum* displayed antifungal activity for stilbenoids of all four structural types. Ten derivatives were tested against five microfungi using the microdilution technique linked with digital image analysis of germ tubes.

The small monocotyledonous family Stemonaceae is classified into three genera: *Stemona*, *Croomia*, and *Stichoneuron*, which are mainly distributed in southeast Asia.[1,2] *Stemona* is the largest genus, with about 25 species, from which *S. tuberosa* Lour., *S. japonica* (Bl.) Miq., and *S. sessilifolia* (Miq.) Miq. have long been used in China and Japan for various medicinal and biological properties. Especially extracts from the fleshy tuberous roots are still used to treat respiratory disorders, including pulmonary tuberculosis and bronchitis, but are also recommended against different insect pests.[3−6] With respect to these various bioactivities little is known about antifungal properties of *Stemona* species. Only Zhao et al.[7] gave the antibacterial and antifungal activity of *S. tuberosa* any but casual notice.

In the course of our joint research project with the Kasetsart University in Bangkok, Thailand, a broad-based phytochemical screening within the Stemonaceae linked with bioassays of the corresponding crude extracts was carried out to discover new biologically active compounds. On the basis of our recent comparison between *S. tuberosa* and *S. collinsae* Craib, the extract from the latter species showed very high insect toxicity against the polyphagous cotton leaf worm *Spodoptera littoralis*.[8] Moreover, in parallel bioautographic tests on TLC plates using conidiospore suspensions of our test fungus *Cladosporium herbarum* (Pers.: Fr.) Link, *S. collinsae* also exhibited pronounced antifungal activity. Especially, methanolic crude extracts from the underground parts, including tuberous roots and rhizomes, were shown to be very active. Whereas the insecticidal activity could be attributed to the accumulation of family-specific alkaloids commonly characterized by a pyrrolo[1,2-*a*]azepin nucleus,[6,8,9] the antifungal property was caused by different groups of stilbenoids. Of special interest was the formation of many rare phenylbenzofurans, which represented the major biogenetic trend of *S. collinsae*. Eleven derivatives were detected that were shown to be hitherto undescribed natural products and designated as stemofurans A−K (**1**−**11**). By contrast, only two stilbenes were found, from which the well-known pinosylvin (**13**) (for further literature see ref 10) was detected in trace amounts only, whereas the rare 4′-methyl derivative (**14**) was accumulated in somewhat larger

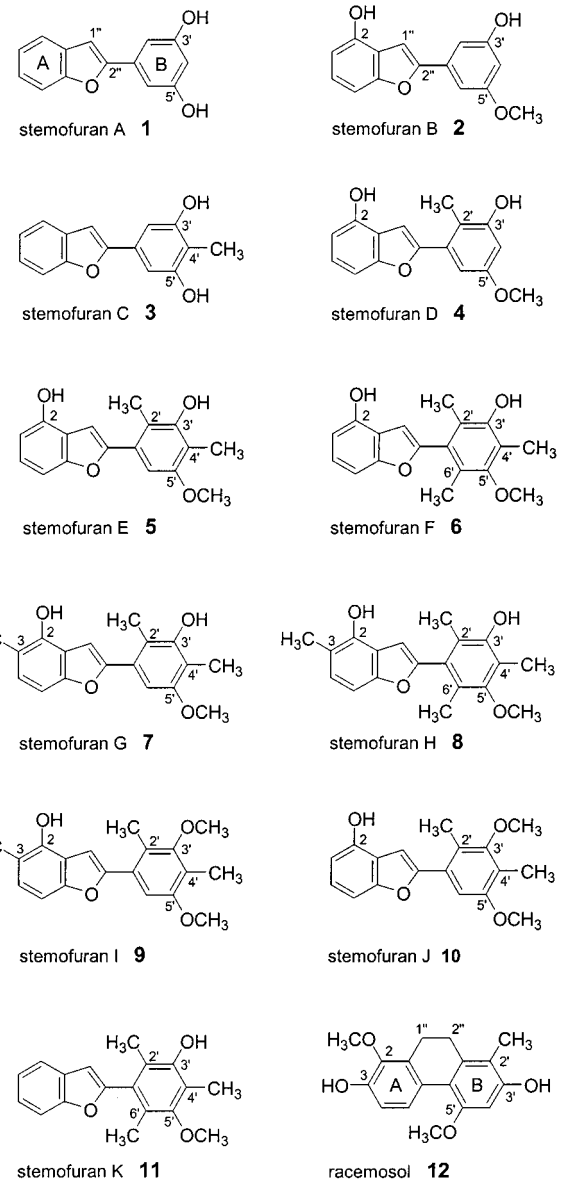

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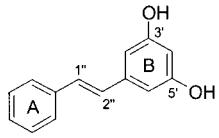
Table 1. ^{1}H NMR of Benzofurans **1**−**11** (acetone-d_6, δ/ppm)[a,b]

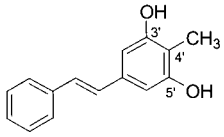
	1[c]	2	3	4	5	6	7	8[d]	9	10	11
2	7.62 dd		7.59 dd								7.52 dd
3	7.23 ddd	6.69 dd	7.22 ddd	6.70 dd	6.69 dd	6.71 dd	2.30 s (Me)	2.31 s (Me)	2.30 s (Me)	6.71 dd	7.27 ddd
4	7.30 ddd	7.12 dd	7.27 ddd	7.15 dd	7.13 dd	7.12 dd	7.05 d	7.04 d	7.06 d	7.15 dd	7.31 ddd
5	7.52 ddd	7.05 ddd	7.50 ddd	7.07 ddd	7.06 ddd	7.03 ddd	6.98 dd	6.96 dd	6.99 dd	7.07 ddd	7.67 ddd
2′	6.93 d	7.00 dd	6.99 s	2.36 s (Me)	2.40 s (Me)	2.08 s (Me)	2.38 s (Me)	2.07 s (Me)	2.41 s (Me)	2.43 s (Me)	2.07 s (Me)
3′									3.72 s (OMe)	3.73 s (OMe)	
4′	6.42 t	6.44 dd	2.14 s (Me)	6.56 d	2.17 s (Me)	2.25 s (Me)	2.17 s (Me)	2.24 s (Me)	2.17 s (Me)	2.17 s (Me)	2.25 s (Me)
5′		3.83 s (OMe)		3.80 s (OMe)	3.87 s (OMe)	3.69 s (OMe)	3.87 s (OMe)	3.69 s (OMe)	3.90 s (OMe)	3.91 s (OMe)	3.69 s (OMe)
6′	6.93 d	6.98 dd	6.99 s	6.90 d	6.94 s	2.06 s (Me)	6.93 s	2.05 s (Me)	7.18 s	7.19 s	2.05 s (Me)
1″	7.16 d	7.27 d	7.03 d	7.09 d	7.03 d	6.80 d	7.10 d	6.84 d	7.18 d	7.10 d	6.76 d

[a] Coupling constants: **1**: $J(2,3) = J(3,4) = 7.7$ Hz, $J(4,5) = 7.9$ Hz, $J(2,4) = J(3,5) = 1.5$ Hz, $J(5,1'') = 0.8$ Hz, $J(2',4') = J(4',6') = 2.2$ Hz; **2**: $J(3,4) = 7.8$ Hz, $J(4,5) = 8.2$ Hz, $J(3,5) = 1.0$ Hz, $J(5,1'') = 0.8$ Hz, $J(2',6') = 1.5$ Hz, $J(2',4') = J(4',6') = 2.3$ Hz; **3**: $J(2,3) = J(3,4) = J(4,5) = 7.6$ Hz, $J(2,4) = J(3,5) = 1.4$ Hz, $J(5,1'') = 0.8$ Hz; **4**: $J(3,4) = J(4,5) = 8.0$ Hz, $J(3,5) = 1.0$ Hz, $J(5,1'') = 0.8$ Hz, $J(4',6') = 2.4$ Hz; **5** and **6**: $J(3,4) = J(4,5) = 7.9$ Hz, $J(3,5) = 1.0$ Hz, $J(5,1'') = 0.9$ Hz; **7** and **8**: $J(4,5) = 8.0$ Hz, $J(5,1'') = 0.8$ Hz; **9**: $J(4,5) = 8.1$ Hz, $J(5,1'') = 0.8$ Hz; **10**: $J(3,4) = J(4,5) = 8.1$ Hz, $J(3,5) = 0.9$ Hz, $J(5,1'') = 0.9$ Hz; **11**: $J(2,3) = J(3,4) = J(4,5) = 7.6$ Hz, $J(2,4) = J(3,5) = 1.5$ Hz, $J(5,1'') = 0.8$ Hz. [b] OH resonances, if identified: **2**: 8.70 vbr s; **3**: 8.28 br s; **4**: 8.46 br s and 8.80 vbr s; **5**: 7.65 vbr s and 8.55 vbr s; **6**: 7.30 vbr s, 8.80 vbr s; **9**: 8.40 br s; **10**: 8.90 br s; **11**: 7.36 br s. [c] Values taken from a mixture **17**:**1**:**13** = 60:25:15%. [d] Values taken from a mixture **7**:**8** = 80:20.

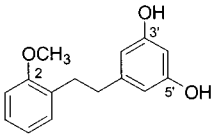
quantities. Furthermore, *S. collinsae* yielded a series of dihydrostilbenes (**15**−**20**) from which **16** and **18** were already previously reported for the roots of *S. tuberosa*,[7] whereas **15**, **17**, **19**, and **20** were shown to be unknown derivatives. Since no trivial names were introduced for **16** and **18**, they were collectively designated here as stilbostemins together with the four new derivatives. The closely related dihydrophenanthrene **12** was previously isolated from *Asparagus racemosus* Willd. by Sekine et al. and named racemosol.[12] However, with respect to an earlier investigation,[13] where the same authors isolated a typical *Stemona* alkaloid from *Asparagus racemosus*, it is to be expected that the roots of *Asparagus* were confused with those of *Stemona*.[8] In addition to stilbenoids, the underground parts of *S. collinsae* also accumulated the tetrahydrofurofuran lignan (+)-sesamin (**21**), coniferyl alcohol (**22**), and large amounts of stigmasterol (**23**). In the present paper we report the isolation and structure elucidation of the new stilbenoids and discuss their possible biogenetic connections. On the basis of germ tube inhibition tests in 2-fold serial broth dilutions against five microfungi, the fungitoxic properties of 10 stilbenoids (dihydrostilbenes, phenylbenzofurans, dihydrophenanthrene) were calculated by image analysis of germinated conidiospores (Table 4).



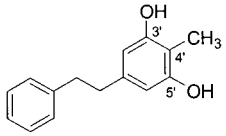
pinosylvin **13**



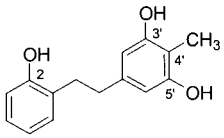
4'-methylpinosylvin **14**



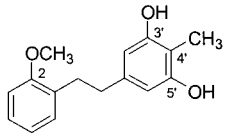
stilbostemin A **15**



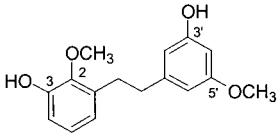
stilbostemin B **16**



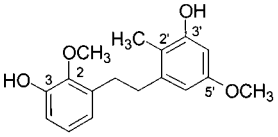
stilbostemin C **17**



stilbostemin D **18**



stilbostemin E **19**



stilbostemin F **20**

Results and Discussion

Air-dried underground parts from *S. collinsae*, collected in southeast Thailand (Chonburi), were extracted with methanol, followed by solvent−solvent partitioning of the aqueous concentrate with chloroform. Subsequent HPLC analysis of the lipophilic crude extract linked with UV detection revealed the occurrence of various groups of phenolics, which were separated by MPLC and TLC. Parallel bioautographic tests on TLC plates with conidiospore suspensions of *Cladosporium herbarum* showed that most of them possessed antifungal activity. Altogether 23 compounds could be isolated, 15 of which were shown to be hitherto unknown derivatives. On the basis of characteristic UV spectra phenylbenzofurans (**1**−**11**), stilbenes (**13**, **14**), and the dihydrophenanthrene **12** with conjugated systems could be clearly distinguished from dihydrostilbenes (**15**−**20**). Similarly, the well-known lignan (+)-sesamin (**21**) and coniferyl alcohol (**22**) were easily detected by their typical spectra. Chromatographic separations of some derivatives were difficult and did not always lead to pure compounds by preparative MPLC and TLC. Apart from mixtures from which pure crystalline compounds could be obtained, e.g., from the pairs **3**/**14**, **5**/**6**, and **7**/**8**, detailed NMR experiments of inseparable derivatives also led to an unambiguous structure elucidation, e.g., in mixture **1**/**13**/**17**.

In *S. collinsae* the new phenylbenzofurans (**1**−**11**) represented the most prominent group of stilbenoids, collectively designated here as stemofurans A−K. Whereas stemofuran A (**1**) together with the highly substituted derivatives **6**−**8**, and **11**, were detected only in small amounts, the new stemofurans B (**2**), C (**3**), E (**5**), I (**9**), and J (**10**) represented major components. Corresponding to the aromatic systems, two main absorption maxima of stemofurans and stilbenes could be distinguished at 291−320 and 204−237 nm (MeOH). However, in the case of compounds **6**, **8**, and **11**, with fully substituted B rings, the strong hypsochromic shift of about 40 nm in **6** and within the pair **7**/**8** indicated nonplanarity and interruption of the conjugation between the two aromatic systems. Dihydrostilbenes clearly deviated by less intense absorption bands in the

Table 2. ^{13}C NMR of Benzofurans **1**−**10** (acetone-d_6, δ/ppm)

	1[a]	**2**	**3**	**4**	**5**	**6**	**7**	**8**[b]	**9**	**10**
1		119.4 s	130.2 s	119.6 s[c]	119.4 s	119.0 s	119.6 s[c]		119.4 s	119.4 s
2	121.9 d	157.2 s	121.7 d	156.7 s[c]	156.9 s	156.4 s	156.8 s[c]		155.1 s	156.8 s
3	124.0 d	108.8 d	123.8 d	108.3 d	108.6 d	108.6 d	117.6 s[c]		117.4 s	108.7 d
4	125.2 d	126.2 d	124.9 d	125.9 d	125.9 d	125.5 d	127.9 d	127.5 d	128.1 d	126.1 d
5	111.7 d	103.5 d	111.6 d	103.2 d	103.5 d	103.6 d	103.1 d	103.2 d	103.1 d	103.4 d
6		152.1 s	155.5 s	151.8 s[c]	151.9 s	151.8 s	148.7 s[c]		148.8 s	152.0 s
1′		133.2 s	129.2 s	132.6 s[c]	129.2 s	130.3 s	129.3 s		129.8 s	129.7 s
2′	104.3 d	105.1 d	104.1 d	115.5 s[c]	116.3 s	123.2 s	116.2 s[c]		121.8 s	121.9 s
3′		159.8 s	157.5 s	157.1 s[c]	155.4 s	152.8 s	155.2 s[c]		159.0 s	159.0 s
4′	104.1 d	102.4 d	113.0 s	102.3 d	114.0 s	120.3 s	114.0 s[c]		120.7 s	120.8 s
5′		162.4 s	157.5 s	159.3 s[c]	157.1 s	157.3 s	157.1 s		157.5 s	157.5 s
6′	104.3 d	102.6 d	104.1 d	105.1 d	103.4 d	121.4 s	103.2 d		106.4 d	106.6 d
1″	102.3 d	100.0 d	101.4 d	103.2 d	103.1 d	104.2 d	103.0 d	104.0 d	103.4 d	103.4 d
2″		155.0 s	157.3 s	154.7 s[c]	155.0 s	154.0 s	155.0 s[c]		154.7 s	154.8 s
3-Me							15.7 q	15.6 q	15.7 q	
2′-Me				12.9 q	13.8 q	14.1 q	13.8 q	14.0 q	13.8 q	13.8 q
4′-Me			8.7 q		9.1 q	9.9 q	9.1 q	9.8 q	9.5 q	9.5 q
6′-Me						13.5 q		13.5 q		
3′-OMe									60.4 q	60.3 q
5′-OMe		55.7 q		55.4 q	56.0 q	60.2 q	55.9 q	60.2 q	56.0 q	56.0 q

[a] Values taken from a mixture **17**:**1**:**13** = 60:25:15%. [b] Values taken from a mixture **7**:**8** = 80:20%. [c] Values of these quaternary carbon atoms were taken from the HMBC spectra and may deviate up to ±0.3 ppm.

Table 3. ^{1}H and ^{13}C NMR of Dihydrostilbenes **15**, **17**,[a] **19**, and **20** ($CDCl_3$,[a] δ/ppm)[b]

	^{1}H				^{13}C[c]			
	15	**17**	**19**	**20**	**15**	**17**[a]	**19**	**20**
1					130.0 s	*d*	*d*	134.9 s
2	3.83 s (OMe)	4.58 br s (OH)	3.77 s (OMe)	3.79 s (OMe)	156.6 s	*d*	*d*	145.8 s
3	6.86 dd	6.75 dd	5.53 s (OH)	5.53 br s (OH)	110.3 d	116.5 d	*d*	149.0 s
4	7.19 ddd	7.08 ddd	6.83 dd	6.84 dd	127.2 d	128.4 d	113.6 d	113.7 d
5	6.88 ddd	6.86 ddd	6.96 dd	6.97 dd	120.4 d	121.0 d	121.4 d	121.4 d
6	7.10 dd	7.10 dd	6.74 dd	6.76 dd	129.8 d	131.5 d	124.9 d	124.9 d
1′					145.6 s	*d*	*d*	142.5 s
2′	6.28 d	6.26 s	6.31 m	2.17 s (Me)	108.1 d	108.2 d	107.8 d	114.0 s
3′	4.76 br s (OH)	4.66 br s (OH)	4.70 br s (OH)	4.70 vbr s (OH)	157.5 s	*d*	*d*	154.6 s
4′	6.19 dd	2.11 s (Me)	6.27 dd	6.28 d	100.3 d	*d*	99.1 d	99.3 d
5′	4.76 br s (OH)	4.66 br s (OH)	3.75 s (OMe)	3.74 s (OMe)	157.5 s	*d*	*d*	158.2 s
6′	6.28 d	6.26 s	6.37 m	6.37 d	108.1 d	108.2 d	106.9 d	107.3 d
1″	2.87 m	2.87 m	2.90 m	2.86 m	32.0 t	33.8 t	31.4 t	30.8 t
2″	2.78 m	2.78 m	2.84 m	2.86 m	36.0 t	37.3 t	36.8 t	35.0 t

[a] The ^{13}C NMR of compound **17** was measured in acetone-d_6 in a mixture **17**:**1**:**13** = 60:25:15%. [b] Coupling constants: **15**: $J(3,4) = 7.9$ Hz, $J(4,5) = J(5,6) = 8.1$ Hz, $J(3,5) = 1.5$ Hz, $J(4,6) = 1.8$ Hz, $J(2'/6',4') = 2.3$ Hz; **17**: $J(3,4) = J(4,5) = J(5,6) = 7.6$ Hz, $J(3,5) = 1.5$ Hz, $J(4,6) = 1.7$ Hz; **19**: $J(4,5) = J(5,6) = 8.4$ Hz, $J(4,6) = 2.0$ Hz, $J(2'/6',4') = 2.3$ Hz; **20**: $J(4,5) = J(5,6) = 8.5$ Hz, $J(4,6) = 2.0$ Hz, $J(4',6') = 2.5$ Hz. [c] Methyl and methoxy resonances in the ^{13}C spectra: **15**: 55.3 q (2-OMe); **17**[a]: 9.1 q (4′-Me); **19**: 61.2 q (2-OMe), 55.3 q (5′-OMe); **20**: 61.3 q (2-OMe), 55.3 q (5′-OMe), 10.4 q (2′-Me). [d] No quaternary C atoms detected due to lack of material.

higher wavelength range between 264 and 280 nm due to the absence of the olefinic C-1″−C-2″ bridge.[14] IR spectra were similar for all stilbenoids (see also ref 14), showing typical signals at 3593−3689 cm^{-1} ($CHCl_3$ or CCl_4) for phenolic hydroxy groups and prominent aromatic signals at 1592−1607 and 1113−1161 cm^{-1}. Compounds with only one aromatic C-methylation at the 4′-position (e.g., **3**, **16**−**18**) were characterized by additional signals at 1624−1628 cm^{-1}.

The ^{1}H NMR spectra of the benzofurans **1**−**11** showed several common features. These compounds are characterized by two independent aromatic systems separated by the furan ring of the benzofuran moiety. In all cases a long-range homoallylic ^4J coupling of ca. 0.8 Hz was observed between 5-H and the isolated 1″-H of the furan ring. Connectivities of directly coupling protons were detected by H/H-COSY, and the positions of the methyl groups in ring A or methyl and methoxy groups in ring B were localized by NOESY experiments. In most cases, even at low concentrations, the phenolic OH groups appeared as broad but clear resonances. C/H correlation spectra and long-range HMBC experiments confirmed the assignments of the structures and allowed the assignment of the quaternary carbon atoms in the ^{13}C NMR spectra. The positions of the OH groups followed indirectly from the ^{1}H coupling pattern of the aromatic rings, the NOESY results, and the positioning of low-field quaternary carbon resonances in the range δ 150−160 (OH and OCH_3 *ipso* C) derived from the HMBC spectra. In some cases the amount of material was not enough to detect the quaternary C atoms directly in the 1D spectra. However, if clear 2D HMBC spectra were available, the resulting chemical shifts of these carbon atoms resulting from relevant cross-peaks were also listed in Table 2.

Although stemofuran A (**1**) was not obtained in pure state, the four-proton system of ring A and the symmetrical ring B with a d (1.5 Hz) for the two *ortho* protons and a t (2.3 Hz) for one *para* proton was rather clear. With two OH groups in *ortho* positions 3′ and 5′, compound **1** was shown to be the parent compound for the whole series, since all compounds **1**−**11** were characterized by 2-fold *ortho* oxygenation (either OH or methylated to OCH_3). Stemofuran B (**2**) was characterized by one methoxy group in ring B and an additional OH substitution at position 2, leaving a three-proton system still showing the 5-H/1″-H long-range coupling for the proton at δ 7.05. Additional C-methylation of stemofuran A (**1**) in *para* position (4′) led to stemofuran C (**3**), whereas stemofuran D (**4**) was derived

Table 4. Germ Tube Inhibition Effect of Stilbenoids from *Stemona collinsae* against Five Microfungi[a]

	Alternaria citri			*Fusarium avenaceum*			*Pyricularia grisea*		
μg/mL	EC_{50} (95% FL)	EC_{90} (95% FL)	MIC	EC_{50} (95% FL)	EC_{90} (95% FL)	MIC	EC_{50} (95% FL)	EC_{90} (95% FL)	MIC
2	5 (3−11)	128 (47−824)	200	10 (3−37)	>200	>200	1.4 (0.5−3)	52 (17−543)	50
16	5 (1−19)	>200 (127−>200)	200	16 (4−226)	>200 (373−>200)	>200	3 (0.1−33)	371 (33−>200)	100
5	5 (2−14)	>200 (143−>200)	>200	18 (6−180)	>200	>200	nd[f]	nd[f]	nd[f]
3	7 (3−15)	528 (145−>200	>200	21 (5−>200)	>200 (492−>200)	>200	3.2 (1.9−5)	30 (16−89)	50
10	50 (24−150)	>200 (446−>200)	>200	32[c]	>200[c]	>200	0.9 (0.6−1.3)	8.5 (5−19)	25
6	10 (3−38)	>200 (274−>200)	>200	np[d]	np[d]	>200	nd[f]	nd[f]	nd[f]
7	14 (6−49)	>200	>200	np[d]	np[d]	>200	nd[f]	nd[f]	nd[f]
18	19 (5−147)	>200 (278−>200)	>200	57 (11−>200)	>200 (350−>200)	>200	3 (1−8)	152 (39−>200)	100
12	25 (4−>200)	>200	>200	240 (24−>200)	>200	>200	42[c]	>200[c]	>200
15	70 (29−392)	>200	>200	>200	>200	>200	46[c]	>200[c]	>200
Benlate[b]	>200	>200	>200	0.02 (0.002−0.1)	>200	100	0.06 (0.02−0.2)	84 (10−>200)	200

	Botrytis cinerea			*Cladosporium herbarum*		
μg/mL	EC_{50} (95% FL)	EC_{90} (95% FL)	MIC	EC_{50} (95% FL)	EC_{90} (95% FL)	MIC
2	8 (0.3−>200)	>200 (229−>200)	>200	183[c]	>200[c]	>200
16	10[c]	>200[c]	>200	15 (5−86)	>200	>200
5	26[c]	>200[c]	>200	0.8 (0.01−5)	>200	>200
3	29 (5−>200)	>200 (195−>200)	>200	8 (3−24)	>200 (112−>200)	>200
10	50 (12−>200)	>200 (554−>200)	>200	34 (6−>200)	>200 (706−>200)	>200
6	np[d]	np[d]	>200	79 (11−>200)	>200	>200
7	np[d]	np[d]	>200	>200	>200	>200
18	11 (4−57)	>200 (316−>200)	>200	17 (5−211)	>200	>200
12	183[c]	>200[c]	>200	>200 (115−>200)	>200	>200
15	np[d]	np[d]	>200	>200 (94−>200)	>200	>200
Benlate[b]	np[e]	np[e]	>200	np[e]	np[e]	>200

[a] 100 μL of stock solution (2 mg of test compound/250 μL of acetone/4.75 mL of 4% malt extract [w/v], emulgated with 0.2% Tween 80) was 2-fold microdiluted in 4% malt extract broth (w/v); negative control, stock solution without test compound. 50 μL of spore suspension (10^4 CFU/mL, 4% malt extract broth [w/v]) was added per well. After incubation for 16 h at room temperature growth was stopped by adding 10 μL of lactophenol blue to each well. Mycelial size was determined by pixel counts after capturing images of 10 germinated conidia per well on a hard disk. Probit-log estimates were calculated from a concentration range of 200−0.1 μg/mL. [b] Positive control; FL, fiducial limits; MIC (minimal inhibitory concentration), lowest concentration showing no conidiospore germination. [c] No fiducial limits can be obtained because of weak germ tube inhibition. [d] np, no probit analysis was possible because of very weak germ tube inhibition of about 30−40% along a concentration range of 1.6−200 μg/mL. [e] np, no probit analysis was possible because of a rather strong inhibition of 85% along a concentration range of 0.4 to 200 μg/mL. [f] nd, not determined.

from stemofuran B (**2**) by a corresponding methylation in *ortho* position (2′). Comparing the different C-methylations in stemofurans **3**−**11**, only stemofuran D (**4**) deviated by a free *para* position (4′). However, strong NOESY cross-peaks between the 5′-OMe group and protons 4′ and 6′ and the effect between 2′-Me and the furan proton 1″ proved unambiguously the structure of stemofuran D (**4**). Stemofuran E (**5**) and stemofuran F (**6**) were characterized by OH groups at positions 2 in ring A and highly substituted B rings. In compound **5** only one proton, a singlet for 6′-H, was left for ring B, which is fully substituted in **6**, showing the characteristic 3′,5′-dioxygenation and 2′,4′,6′-trimethylation. The positions of the 5′-methoxy group and the methyl groups could readily be determined by NOESY experiments. The pair stemofurans G and H (**7**, **8**) differed from **5** and **6** by an additional methyl group at position 3 of ring A (NOESY to 4-H), whereas the B rings were identical. Stemofuran I (**9**) deviated from compound **7** by transformation of 3′-OH to 3′-OCH_3; the same relationship existed between stemofuran J (**10**) and stemofuran E (**5**). Stemofuran K (**11**), with an unsubstituted A ring of the benzofuran system and a fully substituted ring B, was in correlation with compounds **6** and **8**, showing the same B ring pattern. All these relationships are reflected in the ^1H and ^{13}C spectra (Tables 1 and 2).

Besides the chemical shifts and the coupling patterns of the aromatic systems, the ^1H and ^{13}C chemical shifts of the methyl and methoxy groups were of diagnostic value for this series of compounds. In the ^{13}C spectra the resonances for the *para* (4′) methyl groups between two oxygen functions were found at rather high field (δ 8.7−9.9), and for the corresponding *ortho* (2′ and 6′) methyl groups at δ 12.9−14.8. The OMe resonances were found usually at δ 55.4−56.2; however, all OMe groups between two methyl groups showed a downfield shift to δ 60.2−60.4 due to steric compression (5′-OMe for **6** and **8** and 3′-OMe for **9** and **10**). In the chemical shifts of the ^1H NMR spectra a change of conformations due to sterical crowding could be observed. Methoxy groups with two bulky groups as direct neighbors cannot adopt the usually favored planar conformation relative to the aromatic ring, and the chemical shift showed a significant upfield shift to about δ 3.70 caused by a weaker ring current effect (5′-OMe in **6**, **8**, and **11** and 3′-OMe in **9** and **10**). The rotational behavior about the 2″−1′ bond was dramatically changed in compounds **6**, **8**, and **11** with fully substituted B rings: the chemical shifts of 2′-Me in **4**, **5**, **7**, **9**, and **10** (with a proton at *ortho* position 6′) changed from δ 2.36−2.43 to δ 2.05−2.07 for the two *ortho* methyl groups (2′-Me and 6′-Me) in compounds **6**, **8**, and **11**. This steric effect could also be seen in the UV spectra, showing a strong hypsochromic shift of the long-wavelength absorption bands.

The structure elucidation of the new dihydrostilbenes stilbostemins A (**15**), C (**17**), E (**19**), and F (**20**) followed the same strategy using extensive 2D NMR experiments (H/H-COSY, C/H-COSY, NOESY, and HMBC) to identify the substitution patterns of the two isolated aromatic rings. The interpretation of NMR spectra of derivatives **15** and **17** with symmetrically substituted B rings represented no problems at all. For compounds **19** and **20** especially the NOESY cross-peaks allowed a clear decision for the placement of substituents. In **19**, 2-OMe, 6-H, 2′-H, and 6′-H showed interactions with the methylene bridge protons, and in **20**, cross-peaks between 2-OMe, 6-H, 2′-Me, and 6′-H to the methylene protons were found. The position of 5′-OMe in compounds **19** and **20** was clear from cross-peaks

between 5′-OMe and the neighboring protons 4′-H and 6′-H found in the NOESY spectra of both. The ^{13}C assignments of the two methylene bridge carbon atoms of **20** were confirmed by HMBC, showing clear cross-peaks C-1″ to 6-H and C-2″ to 6′-H. The NMR data of the new stilbene derivatives **15**, **17**, **19**, and **20** are compiled in Table 3. In addition to the NMR data the EI-mass spectra were shown to be useful for structure elucidation of this series. The very stable substituted benzylium (tropylium) ions, resulting from breaking the 1″−2″ bond, were representing the most prominent peaks in the spectra, the higher substituted one usually appearing as the base peak.

On the basis of HPLC comparisons of crude extracts from underground parts of different individuals and provenances, collected and prepared in the same way, *S. collinsae* showed marked quantitative variation in the stilbenoid pattern. Especially the accumulation of the inseparable pair of stemofuran C (**3**) and 4′-methylpinosylvin (**14**) varied considerably. Mainly quantitative differences were also observed between leaves, rhizomes, and roots. In this case, the rhizome clearly deviated from the roots by higher concentrations of the already known dihydrophenanthrene racemosol (**12**).[12] The question whether the stilbenoids are induced metabolites, accumulated after microbial infection, was not investigated in the present paper; but with respect to the structurally very similar phytoalexins known from Dioscoreaceae[15] and Orchidaceae,[16] an induced formation at least of some of them can be expected. To establish their role as phytoalexins, a more detailed large-scale analysis of induced roots of *Stemona* species is under way in our laboratory.

The TLC *Cladosporium* bioassay (bioautography) used in the present study permitted an overview of the antifungal activities of the various derivatives. According to that, all four structural types of stilbenoids, stilbenes, dihydrostilbenes, phenylbenzofurans, and dihydrophenanthrenes, possessed antifungal capacities. Using 10 μg for each spot, all samples with the exception of the five stemofurans G−K (**7**−**11**) displayed clear inhibition zones on TLC plates. In the case of compounds **7**−**11**, however, the corresponding spots were more or less overgrown with the fungus, suggesting either weaker activity or decomposition (e.g., **5**, **9**) on TLC plates. To get more detailed antifungal data, 10 stilbenoids were tested in microwells against the four microfungi *Alternaria citri* Ellis & Pierce emend. Bliss & Fawcett, *Fusarium avenaceum* (Corda: Fr.) Sacc., *Pyricularia grisea* (Cooke) Sacc. (teleomorph, *Magnaporthe grisea* Barr), and *Botrytis cinerea* Pers.: Fr. with potential parasitic activity, as well as against the saprophytic *Cladosporium herbarum* (Pers.: Fr.) Link. For all five fungi the spore germination inhibition assay was used and compared with Benlate (50% benomyl) as positive control.[25,26] As shown in Table 4, stemofuran B (**2**) showed the highest antifungal activity against the four parasitic fungi, but only weak effects against *C. herbarum*. High activity was also observed for stemofuran E (**5**) and stilbostemin B (**16**), showing strong antifungal properties even against *C. herbarum* (e.g., EC_{50} of **5** = 0.8 μg/mL). All three derivatives represented major components of the root extract of *S. collinsae*. By contrast, weaker activities were determined for stilbostemin A (**15**) and the dihydrophenanthrene racemosol (**12**), showing EC_{50} values of more than 200 μg/mL against *F. avenaceum* and *C. herbarum*. In general, *P. grisea*, the causative agent of rice blast disease, was shown to be the fungus most susceptible to all stilbenoids (Table 4, e.g., EC_{50} of **10** = 0.9 μg/mL). This higher susceptibility of *P. grisea* against natural fungicides was previously reported for flavaglines.[26] Regarding the already known resistance of *Alternaria* against Benlate (for further literature see ref 26), the observed activities of stilbenoids against *A. citri* underscore the antifungal capacities of these compounds.

Comparing the many stilbenoids already known from the plant kingdom,[10] it became apparent that the stilbenoids of *S. collinsae* can be characterized mainly by two chemical features: (a) the C-methylation of aromatic rings and (b) the formation of phenylbenzofurans. Since the rare aromatic C-methylation was already previously reported for stilbostemins B (**16**) and D (**18**) from *S. tuberosa*,[7] this trend can be expected to be typical for the whole genus. Elsewhere this methylation was only known from *Polygonum lapathifolium*, where the stilbene 4′-methylpinosylvin (**14**) was found to exhibit antidoting activity against the well-known synthetic benzimidazole fungicide benomyl.[11] Similarly, the formation of phenylbenzofurans also has a restricted distribution in plants, only known so far from four families, the Moraceae,[17] Liliaceae,[18] and Gnetaceae.[19,20] However, vignafuran isolated from *Vigna unguiculata* (L.) Walp. of the family Fabaceae[21] cannot be regarded as a stilbenoid, because feeding experiments have shown that it was derived biogenetically from an isoflavonoid precursor.[22] With respect to the co-occurring stilbenes and dihydrostilbenes in *S. collinsae* the stemofurans are most likely derived from a stilbenoid precursor formed via a cinnamoylpolyketide skeleton, as pointed out in ref 17. An important prerequisite for the formation of phenylbenzofurans is an *ortho*-oxygenation at C-2 of the aromatic ring A. Whether this existed already on the level of the cinnamoyl-CoA precursor is still unknown. In this connection it is noteworthy that hydroxylation at C-2 also plays a prominent role in most of the dihydrostilbenes isolated from *S. collinsae*. It remains open whether these dihydrostilbenes are derived by reduction from stilbenes or by the catalytic activity of specific dihydrostilbene synthases from dihydrocinnamoyl precursors.[16] The conversion from dihydrostilbenes to dihydrophenanthrenes is already known from Dioscoreaceae[23] and Orchidaceae[16,24] and can also be predicted for racemosol (**12**), most probably directly derived from stilbostemin F (**20**), which has the same substitution patterns in the aromatic rings A and B. Comparing the structures of stemofurans A−K (**1**−**11**) it became obvious that ring B was most probably formed via the polyketide pathway always showing two oxygen substitutions in *meta* position at C-3′ and C-5′. The aromatic C-methylations were preferently found at the activated position C-4′ and less frequently at C-2′ and C-6′. Moreover, an increasing trend toward O-methylation could be observed in the B ring starting from two free hydroxy groups in **1** and **3**, via one methoxy in **2**, **4**−**8**, and **11**, to two methoxy groups in **9** and **10**. By contrast, ring A, most probably derived from a cinnamoyl precursor, showed a rather simple substitution pattern. Besides the furan-forming oxygen in *ortho* position at C-6, many derivatives (**2**, **4**−**10**) showed an additional hydroxylation in *ortho* position at C-2, suggesting a specific substitution trend toward this particular position.

Experimental Section

General Experimental Procedures. Optical rotation, Perkin-Elmer polarimeter 241; UV, Hewlett-Packard, 8452A diode array spectrophotometer; IR, Perkin-Elmer, 16PC FT-IR; NMR, Bruker AM 400 WB. Standard pulse sequence programs provided by the spectrometer manufacturer were used. The HMBC experiments were optimized for a long-range coupling constant of 8 Hz. The spectra were referenced either to internal TMS (^1H δ 0.00) or to the appropriate solvent

signals ($CDCl_3$ ^1H δ 7.26, ^{13}C δ 77.0, acetone-d_6 ^1H δ 2.05, ^{13}C δ 29.8); MS, Finnigan MAT 900 S; HPLC, Hewlett-Packard 1090II, UV diode array detection at 230 nm, column 150 × 4.6 mm, Phenomenex Synergi Polar-RP80A, 4 μm, mobile phase acetonitrile (gradient 20−60%) in aqueous buffer (0.015 M *o*-phosphoric acid, 0.0015 M tetrabutylammonium hydroxide, pH 3), flow rate 1 mL/min.

Plant Material. Leaves, rhizomes, and roots from *S. collinsae* Craib (Stemonaceae) were collected in southeast Thailand near Chonburi from two different habitats: (a) from Khao Khieo, near Chanthathen waterfall (HG840, HG841, HG842, February 2000); (b) from Sri Racha, coastal slopes with open deciduous forest (HG860, January 2001). Voucher specimens are deposited at the Herbarium of the Institute of Botany, University of Vienna (WU).

Extraction and Isolation. Underground parts from four individuals of *S. collinsae* (HG840−HG842, HG860) were dried for 3−4 weeks and ground separately. The homogenates were extracted with MeOH at room temperature for 5 days, filtered, and concentrated. The aqueous residues were extracted with $CHCl_3$, evaporated to dryness, and dissolved in MeOH. The concentrated MeOH fractions were used as lipophilic crude extracts for comparative HPLC and TLC (Merck Si gel 60, 0.25 mm) sprayed with MeOH−HOAc−H_2SO_4−anisaldehyde reagent (85:10:8:0.5) as well as for bioautographic tests with conidiospore suspensions of *Cladosporium herbarum*. For preparative scale separation, extracts from all individuals were pooled together with those of additional collections from the same habitats (410 g) to amount to 5.4 g of crude extract, which was roughly separated by column chromatography (Merck Si gel 60, 35−70 mesh) using solvent mixtures of increasing polarity (EtOAc in hexane and MeOH) and further by preparative MPLC (400 × 40 mm column, Merck LiChroprep silica 60, 25−40 μm, UV detection, 254 nm) using mixtures of EtOAc in hexane. Preparative TLC (Merck, Si gel 60, 0.5 mm) with mixtures of hexane−Et_2O and $CHCl_3$−MeOH was used to finally purify the compounds. Column fractions eluted with 50%−75% EtOAc in hexane yielded a complex mixture of stilbenoids (1.2 g), which was separated by MPLC using a gradient from 5% to 50% EtOAc in hexane. The obtained fractions were further separated by repeated MPLC with 5%, 10%, and 15% EtOAc in hexane.

Compounds 9 and 11. Fractions eluted with 5% EtOAc in hexane afforded 15 mg of impure **9** and 4 mg of impure **11**. Further purification of **9** followed by crystallization in Et_2O led to 8 mg of pure compound, whereas **11** was separated by preparative TLC (hexane−Et_2O = 4:6) to afford 1 mg of pure compound.

Compounds 10, 16, 21, and 23. Fractions eluted with 10% EtOAc in hexane afforded a mixture of the two stilbenoids **10** and **16** (58 mg) as well as 25 mg (+) of sesamin (**21**) and 60 mg of stigmasterol (**23**), which both crystallized from Et_2O−hexane to yield 8 mg of **21** and 26 mg of **23**. The mixture of stilbenoids was further separated by cyclic MPLC[27] with 10% EtOAc in hexane, leading to 7 mg of **10** and 6 mg of **16**.

Compounds 1−8, 12−15, and 17−20. MPLC with 15% EtOAc in hexane led to five fractions, from which fraction 1 (120 mg) contained **3**, **7**, **8**, and **18**, fraction 2 (96 mg) **5** and **6**, fraction 3 (30 mg) **20**, fraction 4 (125 mg) **1**, **12**, **13**, **17**, and **19**, and fraction 5 (76 mg) **2**, **4**, and **15**. Further separation of fraction 1 with cyclic MPLC[27] using 15% EtOAc in hexane and subsequent preparative TLC (hexane−Et_2O = 4:6) yielded 13 mg of **18** as well as 14 mg of the inseparable pair **3**/**14** and 4.5 mg of **7**/**8** from which 4 mg of **3**, 1 mg of **14**, and 3 mg of **7** were obtained by fractionated crystallization in $CHCl_3$−hexane. MPLC and TLC of fraction 2, using the same solvent systems as in fraction 1, afforded 13 mg of the inseparable pair **5**/**6**, from which 9 mg of **5** was obtained by crystallization and 3 mg of nearly pure **6** from the remaining mother liquor. Fractions 3, 4, and 5 were further separated by cyclic MPLC,[27] like fractions 1 and 2, and by TLC ($CHCl_3$−MeOH = 97:3) to afford 8 mg of **20**, 6 mg of **12**, 2 mg of **19**, and 5 mg of a mixture of **1**/**13**/**17**, from which 0.5 mg of **17** was obtained as pure compound by repeated TLC. Fraction 5 yielded 15 mg of **2** as well as 12 mg of a mixture of **4**/**15**, from which 2 mg of **4** and 4.5 mg of **15** were obtained by final purification on TLC (hexane−Et_2O = 3:7).

Compound 22. MPLC with 50% EtOAc in hexane afforded 45 mg of impure coniferyl alcohol (**22**), which was further separated by TLC (hexane−Et_2O = 1:9) to give 10 mg of pure compound.

Antifungal Bioassay. Authentic samples of test fungi were deposited at the culture collection of the Institute of Applied Microbiology, Agricultural University of Vienna (VIAM): *Alternaria citri* (VIAM MA1627); *Fusarium avenaceum* (VIAM MA1512); *Pyricularia grisea* (VIAM MA1628); *Botrytis cinerea* (VIAM MA2725); *Cladosporium herbarum* (VIAM MA1511). *A. citri*, *F. avenaceum*, *P. grisea*, and *B. cinerea* were grown on 4% potato dextrose agar, and *C. herbarum* was grown on 4% malt extract agar (w/v) at room temperature in darkness. Conidiospores of *A. citri*, *P. grisea*, and *B. cinerea* were harvested after 14 days and those of *F. avenaceum* and *C. herbarum* after 3 days and suspended in a 0.9% NaCl solution (w/v) containing 5% DMSO (v/v). Spores from *A. citri*, *F. avenaceum*, *B. cinerea*, and *C. herbarum* were stored at −30 °C, and those from *P. grisea* at +4 °C. The number of colony-forming units (CFU) were determined by spreading 20 μL of the 10× microdiluted suspension in a Petri dish and by counting germinated spores per dilution. Benlate (50% benomyl) was purchased from Du Pont. Tests were carried out as described in Table 4 and reported previously.[25,26]

Stemofuran A, [2-(3,5-dihydroxyphenyl)benzofuran] (1): FDMS of a mixture **17**/**1**/**13** = 60/25/15% (NMR determination), *m*/*z* 244 (100), 226 (52), 212 (35); HREIMS (70 eV) of the mass at *m*/*z* 226, *m*/*z* 226.0633 (calcd for $C_{14}H_{10}O_3$, 226.0630) for **1**.

Stemofuran B, [2-(3-hydroxy-5-methoxyphenyl)-4-hydroxybenzofuran] (2): white crystals changing to an amorphous structure at 85−90 °C, melting at 176−177 °C; UV (MeOH) λ_{max} (log ϵ) 326 (3.98 sh), 308 (4.26 sh), 298 (4.30), 228 (4.29) nm; IR ($CHCl_3$) ν_{max} 3594 m, 3300 br, 2938 w, 2842 w, 1606 s, 1576 m, 1492 m, 1466 w, 1456 w, 1440 w, 1362 w, 1346 w, 1288 w, 1256 w, 1156 s, 1074 w, 1056 w, 1032 w, 994 w, 976 w, 958 w, 940 w, 870 w, 846 w cm^{-1}; EIMS (70 eV) *m*/*z* 256 (100, M^+), 244 (40), 213 (15), 135 (14), 121 (92), 111 (25), 91 (83), 83 (15), 69 (22), 57 (44); HREIMS *m*/*z* 256.0740 (calcd for $C_{15}H_{12}O_4$, 256.0736).

Stemofuran C, [2-(3,5-dihydroxy-4-methylphenyl)benzofuran] (3): white crystals transformed to long narrow needles at 160−170 °C, melting at 195−197 °C; UV (MeOH) λ_{max} (log ϵ) 320 (4.16), 306 (4.29), 286 (4.10 sh), 278 (3.95 sh), 216 (4.15) nm; IR ($CHCl_3$) ν_{max} 3598 m, 3306 br, 2926 w, 2854 w, 1624 m, 1602 s, 1578 m, 1522 w, 1510 w, 1454 s, 1422 m, 1376 w, 1366 w, 1350 w, 1300 w, 1258 m, 1185 w, 1156 m, 1144 w, 1107 w, 1082 s, 1034 w, 1008 w, 960 m, 939 w, 866 w cm^{-1}; EIMS (70 eV) *m*/*z* 240 (56, M^+), 167 (11), 149 (47), 121 (26), 111 (25), 97 (39), 83 (44), 69 (79), 57 (100); HREIMS *m*/*z* 240.0792 (calcd for $C_{15}H_{12}O_3$, 240.0794).

Stemofuran D, [2-(3-hydroxy-5-methoxy-2-methylphenyl)-4-hydroxybenzofuran] (4): white crystals, mp 144−145 °C; UV (MeOH) λ_{max} (log ϵ) 292 (3.99), 226 (4.05 sh), 216 (4.08) nm; IR ($CHCl_3$) ν_{max} 3596 m, 3308 br, 2928 w, 2852 w, 1604 s, 1496 m, 1466 w, 1456 w, 1443 w, 1424 w, 1360 w, 1336 w, 1288 m, 1180 w, 1154 s, 1116 m, 1034 w, 1010 m, 938 w cm^{-1}; EIMS (70 eV) *m*/*z* 270 (100, M^+), 253 (11), 135 (11), 111 (14), 97 (20), 85 (20), 83 (21), 71 (26), 69 (26), 57 (44); HREIMS *m*/*z* 270.0893 (calcd for $C_{16}H_{14}O_4$, 270.0892).

Stemofuran E, [2-(3-hydroxy-5-methoxy-2,4-dimethylphenyl)-4-hydroxybenzofuran] (5): white crystals transformed to long narrow needles at 130−140 °C, melting at 150−152 °C; UV (MeOH) λ_{max} (log ϵ) 324 (3.36 sh), 306 (3.64 sh), 292 (3.76), 224 (3.86 sh), 214 (3.91) nm; IR ($CHCl_3$) ν_{max} 3598 m, 3292 br, 2939 w, 2841 w, 1605 s, 1581 m, 1492 s, 1464 m, 1455 w, 1439 m, 1413 w, 1383 w, 1360 w, 1336 w, 1289 m, 1254 w, 1241 w, 1154 w, 1124 s, 1028 w, 978 w, 928 w, 896 w, 858 w cm^{-1}; EIMS (70 eV) *m*/*z* 284 (100, M^+), 267 (8), 241 (6), 142 (8), 97 (9), 83 (7), 57 (10); HREIMS *m*/*z* 284.1054 (calcd for $C_{17}H_{16}O_4$, 284.1049).

Stemofuran F, [2-(3-hydroxy-5-methoxy-2,4,6-trimethylphenyl)-4-hydroxybenzofuran] (6): UV (MeOH) λ_{max} (log ϵ) 290 (3.71 sh), 258 (3.85), 220 (4.26 sh), 204 (4.35); IR (CCl_4) ν_{max} 3609 m, 2926 m, 2854 m, 1605 m, 1591 w, 1496 m, 1456 m, 1443 s, 1411 w, 1378 w, 1360 w, 1333 w, 1314 w, 1289 m, 1272 w, 1250 w, 1222 m, 1190 w, 1166 w, 1137 m, 1114 s, 1050 w, 1027 m, 1004 w, 979 w, 916 w cm^{-1}; EIMS (70 eV) *m/z* 298 (100, M^+), 284 (22), 267 (12), 179 (21), 165 (15), 149 (28), 125 (17), 109 (24), 97 (35), 83 (38), 69 (54), 57 (68); HREIMS *m/z* 298.1205 (calcd for $C_{18}H_{18}O_4$, 298.1205).

Stemofuran G, [2-(3-hydroxy-5-methoxy-2,4-dimethylphenyl)-4-hydroxy-5-methylbenzofuran] (7): fine white needles transformed to long narrow needles at 185−190 °C, melting at 201−202 °C; UV (MeOH) λ_{max} (log ϵ) 326 (3.90 sh), 296 (4.38), 214 (4.40) nm; IR ($CHCl_3$) ν_{max} 3600 m, 3329 br, 2925 m, 2855 w, 1615 w, 1604 m, 1580 w, 1486 s, 1464 m, 1442 w, 1416 w, 1383 w, 1347 w, 1337 w, 1295 w, 1242 m, 1142 w, 1126 s, 1069 w, 1021 w, 995 w, 979 w, 940 w, 922 w, 890 w cm^{-1}; EIMS (70 eV) *m/z* 298 (100, M^+), 281 (23), 255 (16), 165 (16), 149 (28), 97 (22), 83 (25), 69 (33), 57 (50); HREIMS *m/z* 298.1206 (calcd for $C_{18}H_{18}O_4$, 298.1205).

Stemofuran H, [2-(3-hydroxy-5-methoxy-2,4,6-trimethylphenyl)-4-hydroxy-5-methylbenzofuran] (8): FDMS of a mixture **7**/**8** = 79:21% (NMR determination), *m/z* 298 (100), 312 (26); HREIMS (70 eV) of the mass at *m/z* 312, *m/z* 312.1360 (calcd for $C_{19}H_{20}O_4$, 312.1362).

Stemofuran I, [2-(3,5-dimethoxy-2,4-dimethylphenyl)-4-hydroxy-5-methylbenzofuran] (9): white crystals, mp 180−182 °C; UV (MeOH) λ_{max} (log ϵ) 328 (4.00 sh), 312 (4.25 sh), 298 (4.36), 218 (4.42) nm; IR ($CHCl_3$) ν_{max} 3685 w, 3594 w, 3324 br, 2933 w, 2852 w, 1603 s, 1579 w, 1491 w, 1480 s, 1465 m, 1441 w, 1380 w, 1348 w, 1326 w, 1276 w, 1178 w, 1142 m, 1120 s, 1070 w, 998 w, 982 w, 938 w, 911 w, 853 w cm^{-1}; EIMS (70 eV) *m/z* 312 (14, M^+), 279 (29), 167 (45), 159 (25), 149 (100), 113 (16), 71 (27), 57 (40); HREIMS *m/z* 312.1365 (calcd for $C_{19}H_{20}O_4$, 312.1362).

Stemofuran J, [2-(3,5-dimethoxy-2,4-dimethylphenyl)-4-hydroxybenzofuran] (10): UV (MeOH) λ_{max} (log ϵ) 326 (4.22 sh), 312 (4.43 sh), 294 (4.52), 222 (4.47) nm; IR (CCl_4) ν_{max} 3600 m, 3417 br, 2993 w, 2933 m, 2851 w, 1605 s, 1578 w, 1496 w, 1483 w, 1464 m, 1451 w, 1441 m, 1391 w, 1362 w, 1329 w, 1287 w, 1277 w, 1255 w, 1237 w, 1193 w, 1172 w, 1141 s, 1123 s, 1051 w, 1030 m, 1002 w, 982 w, 922 w, 882 w, 850 w cm^{-1}; EIMS (70 eV) *m/z* 298 (100, M^+), 284 (22), 165 (35), 149 (28), 127 (17), 98 (7), 81 (5), 71 (7), 57 (17); HREIMS *m/z* 298.1204 (calcd for $C_{18}H_{18}O_4$, 298.1205).

Stemofuran K, [2-(3-hydroxy-5-methoxy-2,4,6-trimethylphenyl)benzofuran] (11): UV (MeOH) λ_{max} (log ϵ) 282 (4.27), 276 (4.28), 256 (4.41), 204 (4.80); IR (CCl_4) ν_{max} 3614 m, 2986 w, 2927 m, 2853 w, 1582 m, 1558 m, 1453 s, 1412 w, 1378 w, 1348 w, 1333 w, 1303 w, 1291 w, 1277 w, 1256 m, 1232 w, 1220 m, 1191 w, 1169 w, 1150 w, 1134 w, 1113 s, 1005 m, 980 w, 915 w, 886 w, 857 w cm^{-1}; EIMS (70 eV) *m/z* 282 (100, M^+), 265 (25), 251 (16), 167 (33), 97 (20), 83 (43), 69 (28), 57 (63); HREIMS *m/z* 282.1254 (calcd for $C_{18}H_{18}O_3$, 282.1256).

Racemosol, [2,7-dihydroxy-4,8-dimethoxy-1-methyl-9,10-dihydrophenanthrene] (12): colorless crystals, mp 182−183 °C (brown oil in ref 12); UV, IR, ^1H NMR, ^{13}C NMR, and HREIMS, see ref 12.

Stilbostemin A, [1-(3,5-dihydroxyphenyl)-2-(2-methoxyphenyl)ethane] (15): UV (MeOH) λ_{max} (log ϵ) 278 (3.47 sh), 274 (3.48), 224 (4.04 sh), 214 (4.17) nm; IR ($CHCl_3$) ν_{max} 3596 m, 3320 br, 2928 w, 2836 w, 1602 s, 1494 s, 1466 m, 1438 w, 1348 w, 1330 w, 1292 w, 1244 s, 1178 w, 1158 m, 1146 m, 1110 w, 1034 w, 1015 w, 998 w, 972 w, 920 w, 847 w cm^{-1}; EIMS (70 eV) *m/z* 244 (48, M^+), 123 [(17, $C_7H_5(OH)_2^+$, dihydroxytropylium)], 121 [(100, $C_7H_6(OCH_3)^+$, methoxytropylium)], 91 (67), 57 (45); HREIMS *m/z* 244.1102 (calcd for $C_{15}H_{16}O_3$, 244.1099).

Stilbostemin B, [1-(3,5-dihydroxy-4-methylphenyl)-2-phenylethane] (16): white crystals, mp 153−154 °C (76 °C in ref 7); UV (MeOH) λ_{max} (log ϵ) 280 (3.03 sh), 270 (3.06), 262 (3.02 sh), 216 (4.31) nm; IR ($CHCl_3$) ν_{max} 3600 s, 3328 br, 2926 w, 2860 w, 1628 m, 1592 s, 1520 w, 1496 w, 1454 m, 1432 m, 1326 w, 1278 w, 1260 w, 1186 w, 1160 m, 1134 w, 1076 s, 1040 w, 1014 w, 988 w, 936 w, 873 w, 848 w cm^{-1}; ^1H NMR, ^{13}C NMR, and EIMS, see ref 7.

Stilbostemin C, [1-(3,5-dihydroxy-4-methylphenyl)-2-(2-hydroxyphenyl)ethane] (17): UV (MeOH) λ_{max} 280 (3.10 sh), 274 (3.12), 208 (3.90 sh) nm; IR ($CHCl_3$) ν_{max} 3688 m, 3593 m, 3311 br, 2924 w, 2852 w, 1626 m, 1597 s, 1531 w, 1520 w, 1502 w, 1489 w, 1456 m, 1426 w, 1349 w, 1325 w, 1281 w, 1265 w, 1185 w, 1161 m, 1091 w, 1080 w, 987 w, 928 w, 850 w cm^{-1}; EIMS (70 eV) *m/z* 244 (42, M^+), 137 (100, $C_7H_4(OH)_2$-$(CH_3)^+$, dihydroxymethyltropylium), 107 (58, $C_7H_6(OH)^+$, hydroxytropylium), 91 (37), 69 (32), 57 (63); HREIMS *m/z* 244.1102 (calcd for $C_{15}H_{16}O_3$, 244.1099).

Stilbostemin D, [1-(3,5-dihydroxy-4-methylphenyl)-2-(2-methoxyphenyl)ethane] (18): white crystals, mp 110−112 °C (oil in ref 7); UV (MeOH) λ_{max} (log ϵ) 278 (3.46 sh), 272 (3.50), 216 (4.29) nm; IR ($CHCl_3$) ν_{max} 3602 s, 3336 br, 2928 w, 2860 w, 2836 w, 1628 m, 1596 s, 1590 s, 1516 w, 1494 s, 1464 m, 1456 m, 1438 m, 1326 w, 1290 w, 1242 s, 1178 w, 1162 m, 1134 w, 1110 w, 1078 s, 1050 w, 1034 w, 988 w, 934 w, 898 w, 846 w cm^{-1}; ^1H NMR, ^{13}C NMR, and EIMS, see ref 7.

Stilbostemin E, [1-(3-hydroxy-2-methoxyphenyl)-2-(3-hydroxy-5-methoxyphenyl)ethane] (19): UV (MeOH) λ_{max} (log ϵ) 280 (3.20 sh), 274 (3.22), 212 (3.98) nm; IR ($CHCl_3$) ν_{max} 3689 w, 3536 w, 3300 br, 2928 m, 2854 w, 1600 s, 1497 w, 1488 w, 1472 s, 1436 w, 1349 w, 1332 w, 1286 w, 1178 w, 1158 m, 1072 w, 998 w, 938 w, 924 w, 846 w, 838 w cm^{-1}; EIMS (70 eV) *m/z* 274 (58, M^+), 243 (37, $M^+ - OCH_3$), 137 (100, C_7H_5-$(OH)(OCH_3)^+$, hydroxymethoxytropylium), 109 (73), 91 (23), 69 (18), 57 (40); HREIMS *m/z* 274.1202 (calcd for $C_{16}H_{18}O_4$, 274.1205).

Stilbostemin F, [1-(3-hydroxy-5-methoxy-2-methylphenyl)-2-(3-hydroxy-2-methoxyphenyl)ethane] (20): UV (MeOH) λ_{max} (log ϵ) 278 (3.49), 212 (4.25) nm; IR ($CHCl_3$) ν_{max} 3536 w, 3322 br, 2938 w, 2838 w, 1614 m, 1592 s, 1498 w, 1486 w, 1472 s, 1436 w, 1382 w, 1326 w, 1288 w, 1264 w, 1180 w, 1142 s, 1066 w, 998 w, 962 w, 924 w, 838 w cm^{-1}; EIMS (70 eV) *m/z* 288 (94, M^+), 257 (43, $M^+ - OCH_3$), 151 (96, $C_7H_4(OH)(OCH_3)$-$(CH_3)^+$, hydroxymethoxymethyltropylium), 137 (100, C_7H_5-$(OH)(OCH_3)^+$, hydroxymethoxytropylium), 109 (90), 91 (37), 69 (40), 57 (77); HREIMS *m/z* 288.1362 (calcd for $C_{17}H_{20}O_4$, 288.1362).

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