Stilbenes from the Orchid *Phragmipedium* sp.

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Received January 9, 2007

Three species of *Phragmipedium* (Orchidaceae), *P. calurum*, *P. longifolium*, and *P. hybrid* (var. Sorcerer's Apprentice), were analyzed by high-throughput isolation. A total of 12 new (**1**−**4**, **6**−**10**, **12**, **14**, **16**) and five known compounds (**5**, **11**, **13**, **15**, **17**) were isolated from these orchids. Compounds **1**−**8** are stilbenes substituted with one or two 4-hydroxybenzyl moieties. This type of substitution on stilbenes is unusual and has been reported only twice. The structure elucidation was based on spectroscopic analysis.

Orchidaceae is the largest family of flowering plants, comprising 750 genera and more than 19 000 species.[1] Orchidaceae are known to be a source of a large and diverse variety of secondary metabolites, such as polyphenols, lignans, alkaloids, monoterpenes, triterpenes, and stilbenoids such as phenanthrenes, bibenzyls, and stilbenes to list but a few. Considering the size of the Orchidaceae, only a limited number of phytochemical investigations have been undertaken, and these investigations have produced a few reports describing the natural products of these fascinating plant species. This is most likely due to the fact that Orchidaceae have been underrepresented in most plant-collecting programs, primarily because these herbaceous plants occur in sparse populations and often consist of widely scattered individuals.[2] In order to preserve the botanical diversity of Orchidaceae, the collector has to make sure that each collection will not have a negative impact on the species. It is therefore very difficult to find sufficient material of a species of Orchidaceae that satisfies the quantity requirements of conventional drug discovery programs.[3]

One solution to this problem is to collect orchids that are grown in greenhouses that preserve the genetic material of these species. Moreover, analytical technologies with greater sensitivities are now available to better explore the natural products chemistry of mass-limited biological samples. An example of this new type of technology is the CapNMR probe, which enables the analyses of mass-limited samples. Therefore, a much smaller quantity of plant material is required to prepare the crude plant extract, as microgram amounts of natural product isolated compounds are sufficient to acquire 1D and 2D NMR data.

High-throughput isolation procedures[4] and NMR data collection utilizing the CapNMR probe were used to analyze *Phragmipedium calurum* and *P. longifolium* libraries. *P. calurum* is a hybrid of *P. longifolium* (75%) and *P. schlimii* (25%). These orchids were grown in the greenhouse at the Missouri Botanical Garden (MOBOT). *P. hybrid* was then purchased at a greenhouse in Encinitas, California, which led to additional material for the isolation of interesting stilbenes. *P. hybrid* is an hybrid of *P. longifolium* and *P. lindleyanum*. *P. calurum* yielded seven new (**1**−**4**, **6**, **12**, **14**) and four known (**5**, **11**, **13**, **17**) stilbenes. *P. longifolium* afforded seven new (**1**−**4**, **6**, **10**, **12**) and three known (**5**, **11**, **15**) compounds. Finally, nine new structures were present in *P. hybrid* (**2**, **4**, **6**−**10**, **12**, **16**). Most of these stibenes have unusual substitution patterns.

Results and Discussion

Compound **1** was analyzed by LRESIMS ($[M + H]^+$ *m/z* 333, $[M - H]^-$ *m/z* 331, $[2M - H]^-$ *m/z* 663), HRESIMS *m/z* 333.1496 (calcd for $C_{22}H_{21}O_3$ 333.1491), and NMR as $C_{22}H_{20}O_3$, a formula requiring 13 degrees of unsaturation. The ^{1}H NMR spectrum of **1** displayed resonances of a *trans*-double bond at δ 7.32 and 6.93 (J = 16.1 Hz), aromatic resonances of an unsubstituted phenyl moiety (five protons in the range δ 7.20−7.40), and two *meta*-coupled protons at δ 6.72 and 6.40, characteristic of a substituted phenyl moiety. In addition, one methylene at δ 4.00 as well as a A_2B_2 spin system at δ 7.00 (2H) and 6.64 (2H) could be observed in the ^{1}H NMR spectrum, suggesting the presence of a *p*-substituted aromatic ring. The long-range heteronuclear correlation between the two protons at δ 7.40 (H-2 and H-5) and the carbon at δ 131.1 (C-7) confirmed the linkage between the unsubstituted phenyl moiety and the *trans*-double bond. Moreover, the doublet at δ 7.32 (H-8) showed an HMBC cross-peak with the carbon at δ 103.1 (C-6′) and gave evidence of a double-bond linkage with another phenyl moiety. The latter moiety was substituted with a methoxy group at the C-5′ position on the basis of the HMBC cross-peaks observed from the doublet at δ 6.72 (H-6′) and respectively the methoxy protons at δ 3.80 (OCH_3) to the carbon at δ 160.4 (C5′). Finally the long-distance correlations between the methylene proton at δ 4.00 and the carbon resonances at δ 139.9 (C-1′), 120.4 (C-2′), 157.7 (C-3′), and 130.3 (C-3″ and C-5″) were in accordance with a 4-hydroxybenzyl substituent at C-2′, as well as the position of a hydroxy group at C-3′. The structure was elucidated as a new natural product, (*E*)-3′-hydroxy-2′-(4-hydroxybenzyl)-5′-methoxystilbene.

The ^{1}H NMR of **2** was similar to that of **1**, with only slight differences, suggesting **2** to be similar to **1**. In the positive HRESIMS, compound **2** exhibited $[M + H]^+$ ions at *m/z* 333.1491 (calcd for $C_{22}H_{21}O_3$ 333.1491) and was in accordance with the molecular formula $C_{22}H_{20}O_3$ for **2**. The ^{13}C NMR data of **2** were also similar to those of **1**. The structure of **2** could be determined on the basis of the long-distance correlation between the carbon resonance at δ 160.5 and the methylene protons at δ 3.98, as well as the methoxy group at δ 3.78, which gave evidence of the methoxy group being on C-3′. All the other HMBC correlations where similar to that observed for **1**, suggesting the rest of the molecule to be similar. Compound **2** was then elucidated as the new natural product (*E*)-5′-hydroxy-2′-(4-hydroxybenzyl)-3′-methoxystilbene.

The molecular formula of compound **3** was determined as $C_{22}H_{20}O_4$ from its HRESIMS spectrum (*m/z* 349.1445 $[M + H]^+$, calcd for $C_{22}H_{21}O_4$ requires 349.1440). The ^{1}H NMR and COSY data were characteristic of a stilbene substituted with a hydroxybenzyl moiety. The ^{13}C NMR data of **3** were similar to those of **1**. Differences were seen in the carbon chemical shifts of ring A, suggesting it to be substituted with a hydroxy group. The molecular formula of **3** was in accordance with this hypothesis. In the ^{1}H NMR spectrum, the spin system observed for ring A protons suggested the hydroxy to be at C-2 or C-3. The HMBC cross-peaks

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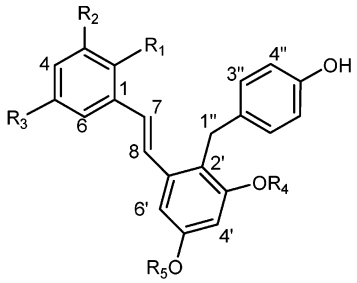
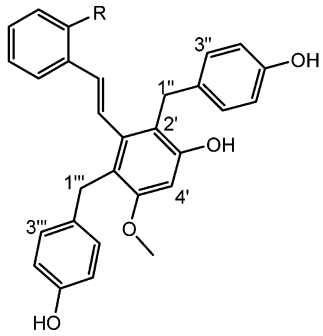
10.1021/np070014j CCC: $37.00
Published on Web 05/31/2007

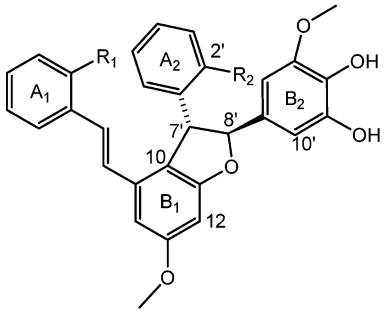
Chart 1



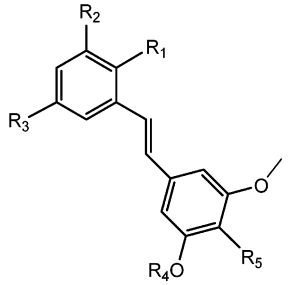
1 R_1=R_2=R_3=R_4=H, R_5=CH_3
2 R_1=R_2=R_3=R_5=H, R_4=CH_3
3 R_1=OH, R_2=R_3=R_4=H, R_5=CH_3
4 R_1=OH, R_2=R_3=R_5=H, R_4=CH_3
7 R_1=R_2=OH, R_3=H, R_4=R_5=CH_3
8 R_1=OH, R_2=R_5=H, R_3=OCH_3, R_4=CH_3



5 R=H
6 R=OH



9 R_1=H, R_2=OH
10 R_1=OH, R_2=H



11 R_1=R_2=R_3=R_5=R_4=H
12 R_1=OH, R_2=R_3=R_4=R_5=H
13 R_1=OH, R_2=R_3=R_5=H, R_4=CH_3
14 R_1=R_2=OH, R_3=R_5=H, R_4=CH_3
15 R_2=OH, R_1=R_3=R_4=R_5=H
16 R_1=OH, R_2=H, R_3=OCH3, R_4=R_5=H
17 R_1=R_2=R_3=R_4=H, R_5=OH

between H-6 at δ 7.33 and carbons at δ 156.0 (C-2) and 126.3 (C-8) confirmed the position of the hydroxy group at C-2. Additional HMBC correlations between the proton at δ 3.98 and carbons at δ 140.6 (C-1′), 120.3 (C-2′), 157.6 (C-3′), 134.3 (C-2″), and 130.4 (C-3″, C-7″), as well as between the methoxy group at δ 3.80 and the carbon at δ 160.2, confirmed the position of the methoxy group at C-5′ and the hydroxy moiety at C-3′. Compound **3** was a new natural product, (*E*)-2,3′-dihydroxy-2′-(4-hydroxybenzyl)-5′-methoxystilbene.

Compound **4** was analyzed by HRESIMS ($[M + H]^+$, *m*/*z* 349.1463, calcd for $C_{22}H_{21}O_4$ 333.1440) and NMR as $C_{22}H_{20}O_4$, a formula requiring 13 degrees of unsaturation. The ^{1}H NMR and ^{13}C NMR spectra of **4** displayed resonances similar to those observed for **3**. The only noticeable difference was in the chemical shifts for C-4′ (δ 99.4) and C-6′ (δ 105.1), a difference similar to that observed between compounds **1** and **2**. This indicated compound **4** to be a stilbene substituted with a methoxy group at C-3′, two hydroxy groups at C-2 and C-5′, and a 4-hydroxybenzyl moiety at C-2′. The position of the methoxy group at C-3′ was confirmed by the HMBC correlation between the carbon at δ 160.3 and protons at δ 3.96 and 3.78, respectively. The HMBC correlations were in accordance with the new structure elucidated for **4**, (*E*)-2,5′-dihydroxy-2′-(4-hydroxybenzyl)-3′-methoxystilbene.

Compound **6** was analyzed by HRESIMS ($[M - H]^-$, *m*/*z* 453.1660, calcd for $C_{29}H_{25}O_5$ 453.1702) and NMR as $C_{29}H_{26}O_5$. The ^{1}H NMR spectrum showed resonances typical of a substituted stilbene. Furthermore, the molecular formula suggested the presence of two hydroxybenzyl moieties. Indeed, the ^{1}H NMR did show two methylene proton resonances at δ 3.90 and 3.93, as well as two A_2B_2 spin systems at respectively δ 6.94 and 6.60, and δ 6.87 and 6.59. The HMBC correlation between the methylene at δ 3.90 and carbons at δ 120.7 (C-2′), 130.3 (C-3″, C-7″), 134.7 (C-2″), 142.9 (C-1′), and 158.6 (C-3′) gave evidence of the position of the hydroxybenzyl moiety at C-2′ and the methoxy group at C-3′. Similar long-range heteronuclear correlations with the other methylene at δ 3.93 determined the position of the other hydroxybenzyl substituent at C-6′ and the hydroxy group at C-5′. Finally, the spin system for ring A was similar to the one observed in compounds **3** and **4**, suggesting the hydroxy group to be at C-2. This was confirmed by the correlation in the HMBC spectrum between the proton at δ 7.09 and the carbons at δ 156.6 (C-2), and 129.1 (C-4), as well as between the adjacent proton at δ 6.73 and the carbons at δ 125.4 (C-1) and 116.4 (C-3). Thus **6** was identified as a new natural product, (*E*)-2,3′-dihydroxy-2′,6′-bis(4-hydroxybenzyl)-5′-methoxystilbene.

The ^{1}H NMR spectrum of **5** was similar to that of compound **6**. Compound **5** was analyzed by HRESIMS ($[M - H]^-$, *m*/*z* 437.1770, calcd for $C_{29}H_{25}O_4$ 437.1753) for $C_{29}H_{26}O_4$, suggesting **5** to have one less hydroxy group than **6**. In the ^{1}H NMR spectrum of **5** we observed the typical spin system of a nonsubstituted phenyl ring. However the ^{13}C NMR chemical shifts were similar to those observed for **6**. The structure of **5** was then elucidated as the known compound previously isolated from the rhizomes of *Galeola faberi*. The chemical shifts recorded in acetone-d_6 were in accordance with the data published.[5] Compound **5** was thus (*E*)-3′-hydroxy-2′,4′-bis(4-hydroxybenzyl)-5′-methoxystilbene.

Compound **7** was analyzed by HRESIMS ($[M - H]^-$, *m*/*z* 377.1412, calcd for $C_{23}H_{21}O_5$ 377.1389) and NMR data as

$C_{23}H_{22}O_5$. The ^{1}H NMR spectrum of **7** showed resonances characteristic of a substituted stilbene. One hydroxybenzyl moiety and two methoxy groups were evident from the ^{1}H NMR data. The molecular formula suggested the presence of two additional hydroxy groups on the stilbene. The hydroxybenzyl substituent was shown to be attached at C-2′ by observation of an HMBC correlation between the methylene protons at δ 3.98 and the carbons at δ 140.2 (C-1′), 121.7 (C-2′), and 160.3 (C-3′). An additional HMBC cross-peak between the methoxy group at δ 3.85 and the carbon resonance at δ 160.3 confirmed the position of the methoxy group at C-3′. Similar HMBC cross-peaks were seen between the methoxy group at δ 3.80 as well as the proton at δ 6.83 (H-14) and the carbon at δ 160.3 (C-13), which confirmed the methoxy group at C-5′. Finally the *ortho*-dihydroxyphenyl moiety was clearly visible with three protons at δ 6.87 (1H, d, $J = 7$ Hz, H-6), 6.67 (1H, d, $J = 6.7$ Hz, H-4), and 6.63 (1H, ov, H-5). The position of the two hydroxy substituents on that ring was confirmed at C-2 and C-3 on the basis of the HMBC correlations between H-7 at δ 7.28 and the carbon resonances at δ 118.7 (C-6) and 145.0 (C-2). Compound **7** is thus the new natural product (*E*)-2,3-dihydroxy-2′-(4-hydroxybenzyl)-3′,5′-dimethoxystilbene.

Compound **8** was analyzed by HRESIMS ($[M + H]^+$, *m*/*z* 379.1556, calcd for $C_{23}H_{23}O_5$ 379.1545) and NMR data as $C_{23}H_{22}O_5$. The ^{1}H NMR data were characteristic of a stilbene substituted with one hydroxybenzyl and two methoxy moieties. Moreover, the molecular formula suggested the presence of two additional hydroxy substituents. The ^{1}H and ^{13}C NMR chemical shifts were similar to those observed in compound **4**, except for the ring A spin system. The ^{1}H NMR data of **8** showed an ABX system with three protons at δ 6.65 (1H, m, H-4), 6.70 (1H, d, $J =$ 8.7 Hz, H-3), and 6.84 (1H, $J = 2.9$ Hz, H-6), suggesting the presence of a disubstituted aromatic ring. The long-distance heteronuclear correlation between H-7 (δ 7.20) and C-2 (δ 150.4) and C-6 (δ 111.7) suggested the presence of a hydroxy group at C-2. Moreover, the coupling constant of 2.9 Hz observed for H-6 at δ 6.84 suggested C-5 to be substituted as well. A methoxy moiety appeared to be at C-5 on the basis of the HMBC cross-peaks observed between the proton at δ 6.70 (1H, d, $J = 8.7$ Hz) and carbons at δ 126.3 (C-1) and 154.2 (C-5), respectively, as well as between the methoxy group at δ 3.72 (OCH_3-1) and the carbon at δ 154.2 (C-5). Other HMBC correlations confirmed the rest of structure **8** to be similar to compound **4**. Thus, the structure of **8** could be elucidated as the new natural product (*E*)-2-hydroxy-2′-(4-hydroxybenzyl)-5,3′,5′-dimethoxystilbene.

Compound **9** was analyzed by HRESIMS ($[M + H]^+$, *m*/*z* 481.1631, calcd for $C_{30}H_{25}O_6$ 481.1651) and NMR data as $C_{30}H_{26}O_6$, corresponding to a stilbene dimer substituted with three hydroxy and two methoxy moieties. The ^{1}H NMR data of compound **9** did show characteristics of a stilbene dimer with the two doublets of a *trans*-double bond at δ 6.82 ($J = 16.4$ Hz, H-8) and 6.93 ($J = 16.4$ Hz, H-7), two coupled doublets at δ 5.46 ($J =$ 4.1 Hz, H-8′) and 5.04 ($J = 4.1$ Hz, H-7′) for a disubstituted dihydrobenzofuran moiety, five protons between δ 7.10 and 7.30 for a nonsubstituted phenyl moiety (ring A_1), two *meta*-coupled doublets at δ 6.48 and 6.76 for ring A_2, four coupled protons at δ 6.75, 6.81, 6.87, and 7.06 for ring B_1, and two *meta*-coupled protons at δ 6.55 and 6.63 for ring B_2. The ^{13}C−^{1}H long-range correlations between H-7/C-2(6) (δ_C 127.6), H-8/C-14 (δ_C 102.1), CH_3-15/C-13 (δ_C 162.8), H-4′ (6′)/C-2′ (δ_C 155.7), H-3′/C-1′ (δ_C 131.0), H-14′/C-8′ (δ_C 94.0), H-10′/C-11′ (δ_C 149.6), and CH_3-15′/C-11′ (δ_C 149.6) allowed the connection as indicated. The relative configuration of H-7′ and H-8′ was deduced to be *trans* on the basis of the NOESY correlations seen between H-7′/H-10′ (14′) and H-8′/H-6′. Thus **9** was determined as a stilbene dimer consisting of two different units: 3-hydroxy-5-methoxystilbene (**11**) and 5′-methoxy-2,3′,4′-trihydroxystilbene. Compound **9** is a new natural product that was given the trivial name phragmidimer A.

The molecular formula of $C_{30}H_{26}O_6$ was established for **10** by HRESIMS ($[M - H]^-$, *m*/*z* 481.1611 calcd for $C_{30}H_{25}O_6$ 481.1651). This molecular formula was the same as for **9** and on the basis of the ^{1}H NMR data presumably also a stilbene dimer but with a different substitution pattern. The ^{13}C NMR chemical shifts of **10** for rings A_2 and B_2 were similar to those of **9** and confirm these rings to have the same substitution pattern. However, the ^{13}C NMR spectrum did show differences in the resonances of C-7 (δ_C 126.0), C-8 (δ_C 125.9), C-7′ (δ_C 58.3), and C-8′ (δ_C 95.5), suggesting a different substitution pattern of rings A_1 and B_1. The HMBC correlations between the proton at δ 7.20 (H-2′) and C-7′ at δ 58.3 confirmed the nonsubstituted phenyl moiety to be linked to the *trans*-double bond (ring A_2). Other HMBC correlations between the proton at δ 7.26 (H-7) and carbons at δ 127.3 (C-6) and 156.1 (C-2) confirmed the position of one hydroxy group at C-2. The relative configuration of H-7′ and H-8′ was deduced to be *trans* on the basis of the NOESY correlations seen between H-7′/H-10′ (14′) and H-8′/H-2′ (6′). Compound **10** was determined as a stilbene dimer consisting of two different units: 2,3′-dihydroxy-5′-methoxystilbene (**12**) and 3,4-dihydroxy-5-methoxystilbene (**17**). Compound **10** is a new natural product that was given the trivial name phragmidimer B.

Compound **12** was analyzed by HRESIMS ($[M - H]^-$, *m*/*z* 241.0840 calcd for $C_{15}H_{13}O_3$ 241.0865) and NMR data as $C_{15}H_{14}O_3$, a formula requiring four degrees of unsaturation. The molecular weight of 242 was in accordance with a stilbene substituted with one methoxy and two hydroxy groups. One ring bears one hydroxy at C-2 on the basis of the HMBC correlation between H-7 (δ 7.39) and carbons at δ 155.6 (C-2) and 127.5 (C-6). The other hydroxy and the methoxy group were, respectively, at C-3′ and C-5′, on the basis of the HMBC correlation between H-8 (δ 7.03) and carbons at δ 106.7 (C-4′) and 104.4 (C-2′). Compound **12** was elucidated as 2,3′-dihydroxy-5′-methoxystilbene, a new natural product.

The ^{1}H NMR of **14** showed all the characteristics of a stilbene substituted with two methoxy and two hydoxyl groups. Its molecular formula, $C_{16}H_{16}O_4$, was deduced from the HRESIMS data ($[M - H]^-$, *m*/*z* 271.0944 calcd for $C_{16}H_{15}O_4$ 271.0970). In the ^{1}H NMR spectrum, three adjacent aromatic protons at δ 7.05 (1H, brt, H-6) and 6.67 (2H, m, H-4, H-5) were in accordance with the dihydroxy substitution of ring A. This was confirmed by the HMBC correlation between H-8 at δ 7.06 and C-6 at δ 118.6. Since H-2′ and H-6′ are equivalent, the two methoxy groups were deduced to be at C-3′ and C-5′. Thus **14** was confirmed to be the new natural product 2,3-dihydroxy-3′,5′-dimethoxystilbene.

Compound **16** was analyzed by HRESIMS ($[M - H]^-$, *m*/*z* 271.0967 calcd for $C_{16}H_{15}O_4$ 271.0970) and NMR data as $C_{16}H_{16}O_4$. These data suggested the presence of two hydroxy and two methoxy substituents on a stilbene. The ^{13}C NMR data of ring B showed similarity with ring B of compound **12**. The ^{13}C NMR data showed that the A ring was similar to ring A of compound **8**. These observations gave evidence of the position of two hydroxy groups at C-2 and C-3′ and two methoxy groups at C-5 and C-5′. This was confirmed by the long-distance heteronuclear correlations observed, and **16** could be deduced as the new natural product 2,3′-dihydroxy-5,5′-dimethoxystilbene.

On the basis of the NMR data, compounds **11**, **13**, **15**, and **17** were identified as the known compounds 3′-hydroxy-5′-methoxystilbene,[6] 3′,5′-dimethoxy-2-hydroxystilbene,[7] 3,3′-dihydroxy-5′-methoxystilbene (thunalbene),[8] and 3′,4′-dihydroxy-5′-methoxystilbene, respectively.[9] Since the reported NMR data of these compounds were incomplete, the chemical shifts and assignments are reported in Table 3.

Stilbenes substituted with hydroxybenzyl moieties are unusual structures with only two reports of similar compounds.[5,10] Moreover, it is interesting to note that we identified in the same extract nonsubstituted stilbenes as well as more substituted derivatives. Compounds **1**, **2**, **5**, and **9** are indeed substituted compounds derived

Table 1. ^{13}C NMR Chemical Shifts for Compounds **1**−**4** and **6**−**8** (150 MHz, CD_3OD)[a]

position	**1**	**2**	**3**	**4**[b]	**6**	**7**[b]	**8**[b]
1	139.2	139.5	126.2[c]	116.7	125.5	n.d.	126.3
2	127.6	127.5	156.1[d]	156.3	156.6	145.0	150.4
3	129.8	130.1	116.8	116.8	116.5	146.4	117.2
4	128.6	128.7	129.5	129.6	129.1	115.1	115.9
5	129.8	130.1	121.0	120.9	120.7	120.4	154.2
6	127.6	127.5	128.1[e]	127.7	128.6	118.5	111.7
7	131.1	130.7	126.3[c]	126.7	130.3	126.7	126.3
8	128.3	128.4	127.9[e]	127.9	130.4	127.7	127.5
1′	139.9	140.0	140.6	140.4	142.8	140.2	140.3
2′	120.4	120.5	120.3	120.5	120.0	121.7	120.6
3′	157.7	160.6	157.6	160.3	156.5	160.3	160.2
4′	102.0	99.6	101.8	99.4	98.8	98.7	99.2
5′	160.4	158.2	160.2	157.7	158.6	160.0	157.5
6′	103.1	104.9	102.8	105.1	120.7	102.6	104.9
OCH_3-5							56.0
OCH_3-3′		55.9		56.2		55.6	55.9
OCH_3-5′	55.8		55.8		55.9	56.0	
1″	30.9	30.2	31.0	30.8	32.4	30.6	30.7
2″	134.3	134.5	134.3	134.3	134.7	134.1	134.4
3″/7″	130.3	130.4	130.4	130.3	130.3	130.2	130.1
4″/6″	116.1	115.7	116.0	116.0	115.8	115.8	115.9
5″	156.0	156.5	156.2[d]	156.1	156.2	156.1	156.0
1‴					32.4		
2‴					134.7		
3‴/7‴					130.3		
4‴/6‴					115.8		
5‴					156.2		

[a] The spectra were referenced to the solvent peak. n.d. = not determined. [b] The δ_C values were obtained from a combination of HSQC and HMBC correlations. [c,d,e] Interchangeable.

Table 2. ^{13}C NMR Chemical Shifts for Compounds **9** and **10** in CD_3OD[a]

position	**9**	**10**[b]
1	138.6	125.5
2	127.6	156.1
3	129.3	116.6
4	128.6	129.7
5	129.3	120.7
6	127.6	127.3
7	130.8	126.0
8	126.6	125.9
9	135.4	137.1
10	121.7	121.7
11	162.8	162.8[c]
12	96.2	96.2
13	162.8	162.8[c]
14	102.1	103.2
15	55.8	56.2
1′	131.0	144.9
2′	155.7	129.3
3′	116.0	130.1
4′	128.8	128.2
5′	121.1	130.1
6′	129.6	129.3
7′	50.0	58.3
8′	94.0	95.5
9′	131.3	133.6
10′	102.1	107.4
11′	149.6	146.7
12′	134.6	135.2
13′	146.3	149.8
14′	106.9	102.3
15′	56.4	56.7

[a] The spectra were referenced to the solvent peak. [b] The δ_C values are obtained from a combination of HSQC and HMBC correlations. [c] Interchangeable.

from stilbene **11**. In the same manner, compounds **3**, **4**, **6**, and **10** are derived from stilbene **12**. Finally compound **8** is derived from stilbene **16**. All these observations suggest that the 4-hydroxybenzyl moiety is added later onto the stilbenoids by electrophilic substitution. Bibenzyl substituted with 4-hydroxybenzyl moieties have already been described from orchid species.[11] As bibenzyls are dihydroderivatives of stilbenes, this further supports the fact that the 4-hydroxybenzyl moiety is most likely added later onto the stilbenoids by electrophilic substitution.[12]

Table 3. ^{13}C NMR Chemical Shifts for Compounds **11**−**16** in CD_3OD

position	**11**	**12**	**13**	**14**[b]	15	**16**[b]
1	138.9	n.a.[a]	n.a.	n.a.	138.9	126.3
2	127.5	155.6	n.a.	144.7	113.9	150.4
3	129.6	116.9	116.2	146.8	158.1	117.6
4	128.5	129.5	129.4	115.3	115.8	115.8
5	129.6	120.7	121.1	120.3	130.6	154.7
6	127.5	127.5	127.6	118.6	119.4	112.0
7	129.8	125.0	125.4	125.3	129.7	125.5
8	129.8	129.2	129.7	129.5	130.5	129.8
1′	140.8	141.2	n.a.	141.5	141.4	141.6
2′	104.7	104.4	105.4	105.4	104.5	104.7
3′	159.9	n.a.	n.a.	163.2	n.a.	159.8
4′	101.9	101.5	101.1	100.5	101.7	101.9
5′	163.6	162.0	n.a.	163.2	161.7	162.8
6′	107.0	106.7	105.4	105.4	106.8	107.1
OCH_3-5						56.0
OCH_3-3′			55.8	55.6		
OCH_3-5′	55.6	55.5	55.8	55.6	55.0	55.6

[a] n.a. = no cross-peak detected in the HMBC spectrum. [b] The δ_C values were obtained from a combination of HSQC and HMBC correlations. [c] Interchangeable.

The isolation of stilbene derivatives from *P. calurum* is of great chemotaxonomical interest. So far, only one stilbene, thunalbene, has been reported from an Orchidaceae.[8] However, a large variety of stilbenoids, including bibenzyl derivatives, have been described from Orchidaceae species.[11,13] The bibenzyls are closely related to stilbenes but are catalyzed by a bibenzyl synthase that uses substrates of dihydrocinnamoyl-CoA derivatives instead of cinnamoyl-CoA. The increase in production of stilbenoids in orchids was shown to occur in wounded plants and therefore suggests these natural products to be phytoalexins.[14,15]

Experimental Section

General Experimental Procedures. Optical rotation was measured on an AUTOPOL IV automatic polarimeter (Rudolph Research Analytical). NMR spectra were acquired on a Bruker spectrometer at 600 MHz equipped with a 5 μL capillary microcoil probe with a 1.5 μL active volume (Magnetic Resonance Microsensors, Savoy, IL). The compounds were dissolved in 6.5 μL of solvent and injected manually into the NMR flow probe. HRESIMS and LRESIMS were done on an LCT time-of-flight mass spectrometer with an electrospray interface (Waters, Milford, MA).

Semipreparative HPLC isolations were performed on a single channel Beckman HPLC system composed of a Beckman 168 diode array UV detector, Alltech 800 ELSD detector, and Gilson FC-204 fraction collector. A splitter was used to split the flow in 10:90 to the ELSD and fraction collector, respectively. The purifications were completed on an analytic Atlantis column (250 × 4.6 mm, 100 Å, Waters).

Plant Material. Three plant species were extracted: *P. calurum*, *P. longifolium*, and *P. hybrid* (var. Sorcerer's Apprentice). *P. calurum* is a hybrid of *P. longifolium* and *P. sedenii*, which is a hybrid of *P. longifolium* and *P. schlimi*. Therefore, *P. calurum* is 75% *P. longifolium* by heritage, with the other 25% of the genome coming from *P. schlimi*. *P. calurum* and *P. longifolium* were grown in the greenhouse at MOBOT and sent frozen to Sequoia, where it was lyophilized. Voucher specimens of *P. calurum* and *P. longifolium* are kept at the Missouri Botanical Garden (USA). *P. hybrid* (var. Sorcerer's Apprentice) is a hybrid of *P. longifolium* and *P. lindleyanum.* This species was purchased at the Cal Pacific Plants in Encinitas in March 2005.

Extraction and Isolation. *P. calurum*, (25 g dry weight) *P. longifolium* (25 g dry weight), and *P. hybrid* (300 g dry weight) were extracted with EtOH−EtOAc (50:50) to obtain 4.0, 7.4, and 24.1 g extracts, respectively. The first gram of *P. calurum* extract was then separated by flash chromatography as previously described to generate flash fractions 2 to 5.[4,16] Flash fractions 2 to 5 were further separated

by preparative HPLC to provide the *P. calurum* library. Flash 5 was purified using a 60% to 85% MeCN in H_2O method. The remainder of the *P. calurum* extract (3 g) as well as *P. longifolium* and *P. hybrid* extract were separated on an open flash column, using the same solvent as for the *P. calurum* library production, namely, a step gradient from hexane−EtOAc (75:25) to EtOAc 100% and then to MeOH 100% to provide flash fractions 2 to 5. The flash fractions were then further separated by preparative chromatography as described above.

The isolation of individual stilbenes from preparative HPLC fractions 1, 2, and 3 was performed using an analytical C18 Atlantis column (4.6 × 250 mm, 100 Å) and beginning with 38% MeCN isocractic for 5 min followed by a gradient to 43% MeCN + 0.05% TFA in 55 min (method A) or 47% MeCN isocratic (method B). Serial collections done with *P. calurum* afforded 110 μg of compound **1**, 50 μg of **2**, 25 μg of **3**, 15 μg of **4**, 40 μg of **5**, 64 μg of **6**, 350 μg of **11**, 55 μg of **12**, 5 μg of **13**, 35 μg of **14**, and 8 μg of **17**. The fractions of *P. longifolium* afforded 400 μg of compound **1**, 40 μg of **2**, 350 μg of **3**, 350 μg of **4**, 100 μg of **5**, 200 μg of **6**, 400 μg of **10**, 440 μg of **11**, 105 μg of **12**, and 30 μg of **15**. Finally, the fractions of *P. hybrid* gave 320 μg of **2**, 88 μg of **4**, 125 μg of **6**, 640 μg of **7**, 50 μg of **8**, 350 μg of **9**, 800 μg of **10**, 40 μg of **12**, and 360 μg of **16**. All these quantities were estimated on the basis of methods using HPLC/ELSD previously described.[16]

The following retention times were observed for each compound during collections: using method B, *P. calurum* afforded compounds **11** (15.6 min), **2** (16.9 min), **13** (18.3 min), and **1** (19.6 min). The more polar compounds were obtained from *P. calurum* using method A: compounds **12** (13.5 min), **17** (16.2 min), **3** (18.0 min), **4** (19.0 min), **14** (22.0 min), **6** (22.7 min), **11** (33.5 min), and **2** (39.5 min). Using method A, *P. longifolium* afforded **15** (12.0 min), **12** (14.5 min) **3** (18.7 min), **4** (20.0 min), **6** (23.3 min), **11** (34.0 min), **2** (41.1 min), **10** (53.0 min), **5** (54.5 min), and **1** (56.7 min). Using method A, *P. hybrid* afforded **16** (13.0 min), **12** (14.5 min), **8** (18 min), **3** (19.5 min), **4** (20.7 min), **6** (24.3 min), **7** (32.2 min), **9** (54.0 min), and **10** (55.7 min).

(*E*)-3′-Hydroxy-2′-(4-hydroxybenzyl)-5′-methoxystilbene (1): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.40 (2H, d, J = 7.5 Hz, H-2, H-6), 7.32 (1H, d, J = 16.1 Hz, H-8), 7.30 (2H, m, H-3, H-5), 7.20 (1H, t, J = 7.3 Hz, H-4), 7.00 (2H, d, J = 8.4 Hz, H-3″, H-5″), 6.93 (1H, d, J = 16.1 Hz, H-7), 6.72 (1H, d, J = 2.2 Hz, H-6′), 6.64 (2H, d, J = 8.4 Hz, H-4″, H-6″), 6.40 (1H, d, J = 2.2 Hz, H-4′), 4.0 (2H,s, CH_2-1″), 3.80 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 331 [M − H]$^-$, 377 [M + HCOO]$^-$, 663 [2M − H]$^-$, 333 [M + H]$^+$; HRESIMS *m/z* 333.1496 (calcd for $C_{22}H_{21}O_3$ 333.1491).

(*E*)-5′-Hydroxy-2′-(4-hydroxybenzyl)-3′-methoxystilbene (2): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.39 (2H, d, J = 7.5 Hz, H-2, H-6), 7.31 (1H, d, J = 16.0 Hz, H-8), 7.30 (2H, t, J = 7.3 Hz, H-3, H-5), 7.20 (1H, t, J = 7.3 Hz, H-4), 6.94 (2H, d, J = 8.4 Hz, H-3″, H-7″), 6.91 (1H, d, J = 16.2 Hz, H-7), 6.71 (1H, d, J = 2.0 Hz, H-6′), 6.63 (2H, d, J = 8.4 Hz, H-4″, H-6″), 6.42 (1H, d, J = 2.0 Hz, H-4′), 3.98 (2H, s, H-1″), 3.78 (3H, s, OCH_3-3′); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 377 [M + HCOO$^-$]$^-$, 663 [2M − H]$^-$, 333 [M + H]$^+$; HRESIMS *m/z* 333.1491 (calcd for $C_{22}H_{21}O_3$ 333.1491).

(*E*)-2,3′-Dihydroxy-2′-(4-hydroxybenzyl)-5′-methoxystilbene (3): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.37 (1H, d, J = 16.3 Hz, H-8), 7.33 (1H, d, J = 7.2 Hz, H-6), 7.22 (1H, d, J = 16.2 Hz, H-7), 7.03 (3H, m, H-4, H-3″, H-5″), 6.78 (2H, m, H-3, H-5), 6.74 (1H, d, J = 1.9 Hz, H-6′), 6.64 (2H, d, J = 8.4 Hz, H-4″, H-6″), 6.37 (1H, d, J = 2.0 Hz, H-4′), 3.98 (2H, s, H-1″), 3.80 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 347 [M − H]$^-$, 695 [2M − H]$^-$, 349 [M + H]$^+$; HRESIMS *m/z* 349.1445 ($C_{22}H_{21}O_4$ requires 349.1440).

(*E*)-2,5′-dihydroxy-2′-(4-hydroxybenzyl)-3′-methoxystilbene (4): insufficient material was isolated to obtain a UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.35 (1H, d, J = 16.2 Hz, H-8), 7.32 (1H, brd, J = 7.4 Hz, H-6), 7.22 (1H, d, J = 16.2 Hz, H-7), 7.04 (1H, t, 7.1 Hz, H-4), 6.96 (2H, d, J = 8.4 Hz, H-3″, H-7″), 6.77 (2H, m, H-3, H-5), 6.74 (1H, d, J = 2.1 Hz, H-6′), 6.63 (2H, d, J = 8.4 Hz, H-4″, H-6″), 6.40 (1H, d, J = 2.1 Hz, H-4′), 3.96 (2H, s, H-1″), 3.78 (3H, s, OCH_3-3′); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 347 [M − H]$^-$, 349 [M + H]$^+$; HRESIMS *m/z* 349.1463 (calcd for $C_{22}H_{21}O_4$ 333.1440).

(*E*)-3′-Hydroxy-2′,4′-bis(4-hydroxybenzyl)-5′-methoxystilbene (5): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.25 (2H, d, J = 7.5 Hz, H-3, H-5), 7.18 (1H, t, J = 7.4 Hz, H-4), 7.14 (2H, d, J = 7.3 Hz, H-2, H-6), 6.90 (2H, d, J = 8.4 Hz, H-3″, H-7″), 6.85 (1H, d, J = 16.8 Hz, H-8), 6.83 (2H, d, J = 8.5 Hz, 3‴, 7‴), 6.62 (2H, d, J = 7.3 Hz, H-4‴, H-6‴), 6.60 (2H, d, J = 8.2 Hz, H-4″, H-6″), 6.54 (1H, s, H-4′), 6.10 (1H,d, J = 16.5 Hz, H-7), 3.89 (2H, s, H-1″), 3.86 (2H, s, H-1‴), 3.79 (3H, s, OCH_3-5′); LRESIMS *m/z* 347 [M − H]$^-$, 383 [M + HCOO$^-$]$^-$, 439 [M + H]$^+$; HRESIMS *m/z* 437.1770 (calcd for $C_{29}H_{25}O_4$ 437.1753).

(*E*)-2,3′-Dihydroxy-2′,6′-bis(4-hydroxybenzyl)-5′-methoxystilbene (6): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.09 (1H, brd, J = 8.2 Hz, H-6), 7.01 (1H, bdt, J = 8.4 Hz, H-4), 6.94 (2H,d, J = 6.5 Hz, H-3″, H-7″), 6.92 (1H, d, J = 16.8 Hz, H-7), 6.87 (2H, d, J = 8.4 Hz, H-3‴, H-7‴), 6.73 (2H, m, H-3), 6.60 (2H, d, J = 8.0 Hz, H-4″, H-6″), 6.59 (2H, d, J = 8.0 Hz, H-4‴, H-6‴), 6.52 (1H, d, J = 17.0 Hz, H-8), 6.50 (1H,s, H-4′), 3.93 (2H, s, H-1″), 3.90 (2H,s, H-1‴), 3.77 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 455 [M + H]$^+$, 453 [M − H]$^-$; LRESIMS *m/z* 455 [M + H]$^+$, 453 [M − H]$^-$; HRESIMS *m/z* 453.1660 (calcd for $C_{29}H_{25}O_5$ 453.1702).

(*E*)-2,3-Dihydroxy-2′-(4-hydroxybenzyl)-3′,5′-dimethoxystilbene (7): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.38 (1H, d, J = 6.2 Hz, H-8), 7.28 (1H, d, J = 6.2 Hz, H-7), 6.96 (1H, d, J = 8.4 Hz, H-3″, H-7″), 6.87 (1H, d, J = 6.1 Hz, H-6), 6.83 (1H, d, J = 2.1 Hz, H-6′), 6.67 (1H, d, J = 6.7 Hz, H-4), 6.63 (3H, m, H-5, H-4″, H-6″), 6.49 (1H, d, J = 2.1 Hz, H-4′), 3.99 (2H, s, H-1″), 3.85 (3H, s, OCH_3-3′), 3.80 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 377 [M − H]$^-$, 754 [2M − H]$^-$; HRESIMS *m/z* 377.1412 (calcd for $C_{23}H_{21}O_5$ 377.1389).

(*E*)-2-Hydroxy-2′-(4-hydroxybenzyl)-5,3′,5′-dimethoxystilbene (8): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.30 (1H, d, J = 16.2 Hz, H-8), 7.20 (1H, d, J = 16.2 Hz, H-7), 6.97 (1H, d, J = 8.4 Hz, H-3″, H-7″), 6.84 (1H, d, J = 2.9 Hz, H-6), 6.74 (1H, d, J = 2.1 Hz, H-6′), 6.70 (1H, d, J = 8.7 Hz, H-3), 6.65 (1H, m, H-4), 6.64 (2H, d, J = 8.4 Hz, H-4″, H-6″), 6.40 (1H, d, J = 2.1 Hz, H-4′), 3.98 (2H,s, H-1″), 3.79 (3H,s, OCH_3-3′), 3.72 (3H, s, OCH_3-5); ^{13}C NMR (150 MHz, CD_3OD), see Table 1; LRESIMS *m/z* 377 [M − H]$^-$, 379 [M + H]$^+$; HRESIMS *m/z* 379.1556 (calcd for $C_{23}H_{23}O_5$ 379.1545).

Phragmidimer A (9): insufficient material was isolated to obtain UV and IR data; $[\alpha]^{27}_D$ +57 (*c* 0.04, MeOH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.24 (2H, m, H-2, H-6), 7.21 (2H, m, H-3, H-5), 7.14 (1H,t, J = 7.0 Hz, H-4), 7.06 (1H, t, J = 7.4 Hz, H-4′), 6.93 (1H, d, J = 16.4 Hz, H-7), 6.87 (1H, d, J = 8.0 Hz, H-3′), 6.82 (1H, d, J = 16.4 Hz, H-8), 6.81 (1H, m, H-6′), 6.76 (1H, brs, H-14), 6.75 (1H, m, H-5′), 6.63 (1H, brs, H-14′), 6.55 (1H, brs, H-10′), 6.48 (1H, brs, H-12), 5.46 (1H, brd, J = 4.4 Hz, H-8′), 5.04 (1H, brd, J = 3.8 Hz, H-7′), 3.84 (3H, s, H-15), 3.80 (2H, s, H-15′); ^{13}C NMR (150 MHz, CD_3OD), see Table 2; LRESIMS *m/z* 481 [M − H]$^-$, 963 [2M − H]$^-$; HRESIMS *m/z* 381.1631 (calcd for $C_{30}H_{25}O_6$ 481.1651).

Phragmidimer B (10): insufficient material was isolated to obtain UV and IR data; $[\alpha]^{27}_D$ +46 (*c* 0.05, MeOH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.35 (2H, t, J = 7.5 Hz, H-3′, H-5′), 7.26 (2H, m, H-7), 7.20 (2H, brd, J = 7.3 Hz, H-2′, H-6′), 6.98 (1H, brt, J = 7 Hz, H-4), 6.89 (1H, d, J = 5.7 Hz, H-6), 6.79 (1H, d, J = 1.9 Hz, H-14), 6.70 (1H, d, J = 8.1 Hz, H-3), 6.66 (1H, d, J = 16.4 Hz, H-8), 6.63 (1H, t, J = 7.4 Hz, H-5), 6.44 (3H, brs, H-12, H-10′, H-14′), 5.35 (1H, d, J = 6.5 Hz, H-8′), 4.58 (1H, d, J = 6.5 Hz, H-7′), 3.85 (3H, s, CH_3-15), 3.78 (3H, s, CH_3-15′); ^{13}C NMR (150 MHz, CD_3OD), see Table 2; LRESIMS *m/z* 481 [M − H]$^-$, 963 [2M − H]$^-$; HRESIMS *m/z* 381.1611 (calcd for $C_{30}H_{25}O_6$ 481.1651).

3′-Hydroxy-5′-methoxystilbene (11): ^{1}H NMR (600 MHz, CD_3OD) δ 7.51 (2H, d, J = 7.5 Hz, H-2, H-6), 7.33 (2H, d, J = 7.6 Hz, H-3, H-5), 7.22 (1H, t, J = 7.3 Hz, H-4), 7.08 (1H, d, J = 16.4 Hz, H-7), 7.04 (1H, d, J = 16.4 Hz, H-8), 6.60 (2H, brs, H-2′, H-6′), 6.29 (1H, brs, H-4′), 3.78 (3H, s, OCH_3); ^{13}C NMR (150 MHz, CD_3OD), see Table 3; LRESIMS *m/z* 225 [M − H]$^-$, 227 [M + H]$^+$.

2,3′-Dihydroxy-5′-methoxystilbene (12): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.51 (1H, d, J = 7.5 Hz, H-6), 7.39 (1H, d, J = 16.4 Hz, H-7), 7.06 (1H, t, J = 6.8 Hz, H-4), 7.03 (1H, d, J = 16.5 Hz, H-8), 6.81 (2H, m, H-3, H-5), 6.59 (2H, brs, H-2′, H-6′), 6.26 (1H, brs, H-4′), 3.78 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 3; LRESIMS *m/z* 481 [M − H]$^-$, 963 [2M − H]$^-$; HRESIMS *m/z* 241.0840 (calcd for $C_{16}H_{13}O_4$ 241.0865).

3′,5′-Dimethoxy-2-hydroxystilbene (13): ^{1}H NMR (600 MHz, CD_3OD) δ 7.53 (2H, d, $J = 7.4$ Hz, H-6), 7.43 (1H, d, $J = 16.3$ Hz, H-7), 7.08 (1H,d, $J = 16.4$ Hz, H-8), 7.07 (1H, d, $J = 7.1$ Hz, H-4), 6.81 (2H, m, H-3, H-5), 6.70 (2H, d, 2 Hz, H-2′, H-6′), 6.37 (1H, brs, H-4′), 3.80 (6H, s, OCH_3-3′, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 3; LRESIMS *m*/*z* 255 $[M - H]^-$, 257 $[M + H]^+$.

2,3-Dihydroxy-3′,5′-dimethoxystilbene (14): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.44 (1H, d, $J = 16.4$ Hz, H-7), 7.06 (1H,d, $J = 16.4$ Hz, H-8), 7.05 (1H, brt, H-6), 6.69 (2H, s, H-2′, H-6′), 6.67 (2H, m, H-4, H-5), 6.37 (1H, brs, H-4′), 3.81 (6H, s, OCH_3-3′, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 3; LRESIMS *m*/*z* 271 $[M - H]^-$, 273 $[M + H]^+$; HRESIMS *m*/*z* 271.0944 (calcd for $C_{16}H_{15}O_4$ 271.0970).

3,3′-Dihydroxy-5′-methoxystilbene (thunalbene) (15): ^{1}H NMR (600 MHz, CD_3OD) δ 7.15 (1H, t, $J = 7.8$ Hz, H-5), 7.01 (1H, d, $J = 16.2$ Hz, H-8), 7.00 (1H, d, $J = 7.2$ Hz, H-6), 6.98 (1H,d, $J = 16.4$ Hz, H-7), 6.95 (1H, brs, H-2), 6.68 (2H, dd, $J = 7.8$, 1.9 Hz, H-4), 6.59 (1H, brs, H-2′), 6.57 (1H, brs, H-6′), 6.28 (1H, t, $J = 2.1$ Hz, H-4′), 3.78 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 3; LRESIMS *m*/*z* 241 $[M - H]^-$, 287 $[M + HCOO^-]^-$, 243 $[M + H]^+$.

2,3′-Dihydroxy-5,5′-dimethoxystilbene (16): insufficient material was isolated to obtain UV and IR data; ^{1}H NMR (600 MHz, CD_3OD) δ 7.38 (1H, d, $J = 16.4$ Hz, H-7), 7.08 (1H, d, $J = 2.8$ Hz, H-6), 7.02 (1H,d, $J = 16.4$ Hz, H-8), 6.74 (1H, $J = 8.7$ Hz, H-3), 6.68 (2H, dd, $J = 8.7$, 2.9 Hz, H-4), 6.60 (1H, brd, $J = 2.0$ Hz, H-2′), 6.59 (1H, brd, $J = 2.20$ Hz, H-6′), 6.27 (1H, t, $J = 2.0$ Hz, H-4′), 3.78 (3H, s, OCH_3-5), 3.77 (3H, s, OCH_3-5′); ^{13}C NMR (150 MHz, CD_3OD), see Table 3; LRESIMS *m*/*z* 271 $[M - H]^-$, 273 $[M + H]^+$; HRESIMS *m*/*z* 271.0967 (calcd for $C_{16}H_{15}O_4$ 271.0970).

3′,4′-Dihydroxy-5′-methoxystilbene (17): ^{1}H NMR (600 MHz, CD_3OD) δ 7.49 (2H, d, $J = 7.6$ Hz, H-2, H-6), 7.31 (2H, t, $J = 7.8$ Hz, H-3, H-5), 7.19 (1H, t, $J = 7.3$ Hz, H-4), 7.00 (1H, d, $J = 16.3$ Hz, H-8), 6.95 (1H, d, $J = 16.4$ Hz, H-7), 6.71 (1H, brs, H-2′), 6.69 (1H, brs, H-6′), 3.89 (3H, s, OCH_3-5′); LRESIMS *m*/*z* 241 $[M - H]^-$, 287 $[M + HCOO^-]^-$, 243 $[M + H]^+$.

Acknowledgment. Sequoia Sciences gratefully acknowledges J. Stone, A. Bradley, G. Walters, and Dr. J. Miller from Missouri Botanical Garden for providing the plant source of the natural products. The authors thank the University of Mississippi for allowing us to measure the optical rotation of compounds **9** and **10** on their instrument. In addition, the authors thank C. Francis, N.-T. Le, Y.-S. L. Lee, and F. Nekouee for their technical assistance. Finally, the authors would like to acknowledge the scientific collaboration with Advanced Chemistry Development, Inc. (ACD Labs) and the use of ACD/SpecManager and ACD/Structure Elucidator.

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NP070014J