SUPPLEMENTARY MATERIAL

A New 9,10-Dihydrophenanthrene from *Dendrobium moniliforme*

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A new 9,10-dihydrophenanthrene, 1,5-dihydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene (**1**), was isolated and identified from the whole plants of *Dendrobium moniliforme*, as well as twenty-four known compounds including hircinol (**2**), (2*R**,3*S**)-3-hydroxymethyl-9-methoxy-2-(4'-hydroxy-3',5'-dimethoxyphenyl)-2,3,6,7-tetrahydrophenanthro [4,3-*b*] furan-5,11-diol (**3**), diospyrosin (**4**), aloifol I (**5**), moscatilin (**6**), 3,4'-dihydroxy-3',4,5-trimethoxybibenzyl (**7**), gigantol (**8**), 3,3'-dihydroxy-4,5-dimethoxybibenzyl (**9**), longicornuol A (**10**), *N-trans*-cinnamoyltyramine (**11**), paprazine (**12**), *N-trans*-feruloyl 3'-*O*-methyldopamine (**13**), moupinamide (**14**), dihydroconiferyl dihydro-*p*-coumarate (**15**), dihydrosinapyl dihydro-*p*-coumarate (**16**), 3-isopropyl-5-acetoxycyclohexene-2-one-1 (**17**), *p*-hydroxybenzaldehyde (**18**), vanillin (**19**), *p*-hydroxyphenylpropionic acid (**20**), vanillic acid (**21**), protocatechuic acid (**22**), (+)-syringaresinol (**23**), β -sitosterol (**24**) and daucosterol (**25**). Compounds **3**, **4**, **13**, **16**, **17** and **20** were isolated from the *Dendrobium* genus for the first time, and compounds **2**, **5**, **7**, **9-12**, **14**, **15**, **18**, **21** and **22** were originally obtained from *D. moniliforme*.

Keywords: *Dendrobium moniliforme*; Orchidaceae; 9,10-dihydrophenanthrene

Supporting information

Spectroscopic data of the known compounds **2-25**.

Figure S1. Key HMBC (H→C) correlations for **1**

Figure S2. Major ROESY correlations for **1**

Table S1. NMR data of compound **1**

Original spectra of compound **1**.

^1H NMR Spectrum (400 MHz, CD_3OD)

^{13}C NMR Spectrum (100 MHz, CD_3OD)

COSY Spectrum

HSQC Spectrum

HMBC Spectrum

ROESY Spectrum

HREIMS

EIMS

IR

Spectroscopic data of the known compounds **2-25**.

Hircinol (2)

Pale yellow needles. ¹H NMR (400MHz, CD₃OD, δ, ppm, J/Hz): 7.04(1H, t, J=7.9, H-7), 6.80, 6.78 (1H each, both s, H-6, 8), 6.53 (1H, d, J=2.3, H-1), 6.48 (1H, d, J=2.3, H-3), 3.90 (3H, 2- OCH₃), 2.61 (4H, m, 9-CH₂, 10-CH₂); ¹³C NMR (100MHz, CD₃OD, δ, ppm): δ 159.0 (C-2), 156.8 (C-5), 154.4 (C-4), 144.6 (C-10a), 141.9 (C-8a), 128.4 (C-7), 122.1 (C-4b), 120.6 (C-8), 118.3 (C-6), 115.0 (C-4a), 110.0 (C-7), 100.2 (C-3), 57.5 (2- OCH₃), 32.3 (C-9), 32.0 (C-10).

(2R*,3S*)-3-Hydroxymethyl-9-methoxy-2-(4'-hydroxy-3',5'-dimethoxyphenyl)-2,3,6,7-tetrahydrophenanthro[4,3-b]furan-5,11-diol (3)

Yellow oil. ¹H NMR (400MHz, CD₃OD, δ, ppm, J/Hz): 6.90 (1H, s, H-4), 6.69 (2H, s, H-2', 6'), 6.44 (1H, d, J=2.5, H-8), 6.33 (1H, d, J=2.5, H-10), 5.58(1H, d, J=6.6, H-2), 3.85 (2H, m, H-7'), 3.78 (6H, s, 3'- OCH₃, 5'- OCH₃), 3.73 (3H, s, 9- OCH₃), 3.59 (1H, br, q, J=6.1, H-3), 2.82 (1H, m, H-6), 2.65 (2H, m, H-7), 2.56 (1H, m, H-6); ¹³C NMR (100MHz, CD₃OD, δ, ppm): 161.5 (C-9), 156.3 (C-11), 149.7 (C-5), 149.5 (C-3', 5'), 147.6 (C-11c), 143.1 (C-7a), 136.9 (C-4'), 132.7 (C-1'), 127.2 (C-3a), 126. (C-5a), 117.9 (C-11b), 114.2 (C-11a), 111.4 (C-4), 107.7 (C-8), 104.4 (C-2', 6'), 103.2 (C-10), 89.7 (C-2), 64.6 (C-7'), 56.7 (C-3', 5'- OCH₃), 55.6 (C-9- OCH₃), 54.7 (C-3), 31.9 (C-3), 23.3 (C-6).

Diospyrosin (4)

Yellow amorphous powder. ^1H NMR (CD_3OD , 400 MHz): δ 9.56 (1H, d, $J=7.9$ Hz, H-9), 7.60 (1H, d, $J=15.7$ Hz, H-7), 7.27 (1H, s, H-6), 7.22 (1H, s, H-2), 6.93 (1H, d, $J=1.5$ Hz, H-6'), 6.81 (1H, dd, $J=8.1, 1.6$ Hz, H-4'), 6.76 (1H, J=8.1 Hz, H-3'), 6.67 (1H, dd, $J=15.8, 7.9$ Hz, H-8), 5.59 (1H, d, $J=6.4$, H-7'), 3.89 (s, OCH_3), 3.81-3.88 (m, 9'- CH_2), 3.80 (s, OCH_3), 3.54-3.55 (m, H-8'); ^{13}C NMR (CD_3OD , 100 MHz): δ 196.2 (C-9), 156.1 (C-7), 152.9 (C-4), 149.2 (C-5'), 147.8 (C-2'), 146.0 (C-3), 133.9 (C-1'), 131.2 (C-5), 129.6 (C-1), 127.1 (C-8), 120.0 (C-6), 120.0 (C-4'), 116.2 (C-3'), 114.2 (C-2), 110.5 (C-6'), 90.1 (C-7'), 64.5 (C-9'), 56.7 (OCH_3), 56.3 (OCH_3), 54.6 (C-8').

Aloifol I (5)

Yellow oil. EIMS m/z (%): 274 (M^+ , 25), 167 (100), 137 (5), 107 (15), 77 (10); ^1H NMR (CDCl_3 , 400 MHz) δ 7.15 (1H, t, $J=7.8$ Hz, H-5'), 6.74 (1H, d, $J=7.5$ Hz, H-3'), 6.68 (1H, d, $J=1.9$ Hz, H-2'), 6.65 (1H, m, H-6'), 6.38 (2H, s, H-2, 6), 3.85 (6H, s, 3, 5-OMe), 2.84 (4H, H- α , α'); ^{13}C NMR [$(\text{CD}_3)_2\text{CO}$, 100 MHz]: δ 155.7 (C-3'), 146.8 (C-3, 5), 143.5 (C-1'), 132.8 (C-4), 132.7 (C-1), 129.4 (C-5'), 120.8 (C-6'), 115.5 (C-2'), 112.9 (C-4'), 105.1 (C-2, 6), 56.2 (3, 5- OCH_3), 38.0 (C- α'), 37.8 (C- α).

Moscatilin (6)

Yellow oil. EIMS m/z (%): 304 (M^+ , 54), 137 (100), 122 (22), 107 (9), 94 (16), 77 (11); 1H NMR [$(CD_3)_2CD$, 400 MHz]: δ 6.59 (1H, d, $J=8.0$ Hz, H-5'), 6.48 (1H, dd, $J=8.0, 2.0$ Hz, H-6'), 6.45 (1H, d, $J=2.0$ Hz, H-2'), 6.25 (2H, s, H-2, 6), 3.65 (9H, s, 3', 3, 5-OCH₃), 2.65 (4H, m, H- α , α'); ^{13}C NMR [$(CD_3)_2CD$, 100MHz]: δ 149.0 (C-3, 5), 148.6 (C-3'), 145.5 (C-4'), 134.8 (C-1'), 134.5 (C-1), 134.0 (C-4), 122.0 (C-6'), 116.0 (C-5'), 113.5 (C-2'), 106.8 (C-2, 6), 56.7 (C-3, 5-OCH₃), 56.3 (C-3'-OCH₃), 39.6 (C- α), 39.0 (C- α').

3,4'-Dihydroxy-3',4,5-trimethoxybibenzyl (7)

Yellow oil. 1H NMR (CD_3OD , 400 MHz): δ 6.85 (1H, d, $J=8.0$ Hz, H-5'), 6.71 (1H, dd, $J=8.1$ Hz, 1.8 Hz, H-6'), 6.67 (1H, d, $J=1.8$ Hz, H-2'), 6.49 (1H, d, $J=1.8$ Hz, H-6), 6.26 (1H, d, $J=1.7$ Hz, H-2), 3.89 (3H, s, 4-OMe), 3.87 (3H, s, 3'-OMe), 3.84 (3H, s, 3-OMe), 2.86 (4H, m); ^{13}C NMR (CD_3OD , 100 MHz) : δ 152.0 (C-5), 149.0 (C-4'), 146.2 (C-3), 143.7 (C-1', 3'), 138.1 (C-1), 133.6 (C-4), 120.9 (C-6'), 114.2 (C-2'), 111.1 (C-5'), 107.9 (C-2), 104.4 (C-6), 60.9 (C-4-OCH₃), 55.8 (C-3, 3'-OCH₃), 38.3 (C- α), 37.5 (C- α').

Gigantol (8)

Red gum. EI-MS m/z (%): 274 (M^+ , 54), 137 (100), 122 (22), 107 (9), 94(16), 77(11); 1H NMR [$(CD_3)_2CO$, 500 MHz]: δ 6.67 (1H, d, $J= 8.0$ Hz, H-5'), 6.64 (1H, d, $J= 7.8$ Hz, H-2'), 6.58 (1H, dd, $J= 8.0, 1.8$ Hz, H-6'), 6.21-6.16 (3H, m, H-2, H-4, H-6), 3.75 (3H, s, 3'-OMe), 3.67 (3H, s, 3-OMe), 2.76 (4H, m, H- α , H- α'); ^{13}C NMR

[(CD₃)₂CO, 125 MHz]: δ 162.2 (C-3), 159.3 (C-5), 148.6 (C-3'), 145.6 (C-1), 145.6 (C-4'), 134.7 (C-1'), 121.9 (C-6'), 115.9 (C-5'), 113.3 (C-2'), 109.2 (C-6), 106.6 (C-2), 99.8 (C-4), 56.2 (-OCH₃), 55.5 (-OCH₃), 39.6 (C- α), 38.5 (C- α').

3,3'-Dihydroxy-4,5-dimethoxybibenzyl (9)

Colorless oil. EIMS $m/z(\%)$: 274(M⁺, 45), 167 (100), 137 (15), 107 (19), 77 (17). ¹H NMR (CDCl₃, 500 MHz) δ 7.15 (1H, t, J= 7.6 Hz, H-5'), 7.76 (1H, d, J= 7.5 Hz, H-6'), 6.77 (2H, d, J= 6.5 Hz, H-4', 2'), 6.48 (1H, s, H-2), 6.25 (1H, s, H-6), 3.87(3H, s), 3.84 (3H, s), 2.81 (4H, m); ¹³C NMR (CDCl₃, 125 MHz) δ 155.6 (C-3'), 152.1 (C-5), 149.0 (C-3), 143.6 (C-1'), 138.0 (C-1), 133.7 (C-4), 129.5 (C-5'), 120.9 (C-6'), 115.4 (C-2'), 112.9 (C-4'), 107.9 (C-2), 104.5 (C-6); 60.9 (5-OMe), 55.8 (4-OMe), 37.7 (C- α , α').

Longicornuol A (10)

White powder. EIMS $m/z(\%)$: 468 (M⁺), 260, 210, 182, 167, 153, 107, 77. ¹H NMR (CD₃OD, 500 MHz): δ 7.05 (1H, t, J=7.6 Hz, H-5), 6.75 (1H, s, H-19), 6.70 (1H, dd, J=2.0, 1.2 Hz, H-2), 6.67 (1H, dd, J=7.5, 1.2 Hz, H-6), 6.63 (1H, dd, J=7.6, 1.9 Hz, H-4), 6.36 (1H, d, J=1.6 Hz, H-14), 6.33 (1H, d, J=1.6 Hz, H-10), 4.91 (1H, d, J=7.6 Hz, H-21), 4.00 (1H, m, H-22), 3.83 (6H, s, H-25, 26), 3.78 (3H, s, H-24), 3.71 (1H, m, J=12.5, 2.3 Hz, H-23 β), 3.48 (1H, m, J=12.5, 4.4 Hz, H-23 α), 2.80 (4H, m, H-7, 8); ¹³C NMR (CD₃OD, 125 MHz) : δ 158.3 (C-3), 149.7 (C-13), 149.4 (C-16), 149.3 (C-26), 145.5 (C-11), 144.6 (C-1), 137.1 (C-17), 135.9 (C-15), 135.5 (C-9), 132.5

(C-12), 130.2 (C-5), 128.7 (C-20), 120.9 (C-2), 116.5 (C-2), 113.7 (C-4), 110.8 (C-10), 106.3 (C-19), 105.8 (C-14), 79.8 (C-22), 77.8 (C-21), 62.1 (C-23), 56.8 (C-25, 26), 56.6 (C-24), 39.1 (C-7), 39.0 (C-8).

N-trans-Cinnamoyltyramine (11)

White powder. EIMS $m/z(\%)$: 267 (M^+ , 30), 148 (65), 131 (95), 120 (100), 103 (36), 77 (24). 1H NMR (CD_3OD , 500 MHz): δ 7.05 (2H, d, $J=8.3$ Hz, H-2, 6), 6.71 (2H, d, $J=8.4$ Hz, H-3, 5), 7.52 (3H, m, H-2', 6', 7'), 7.37 (3H, m, H-3', 4', 5'), 6.57 (1H, d, $J=15.8$ Hz, H-8'), 3.47 (2H, t, $J=7.3$ Hz, H-8), 2.76 (2H, t, $J=7.3$ Hz, H-7); ^{13}C NMR (CD_3OD , 125 MHz) : δ 168.6 (C-9), 157.0 (C-4), 141.6 (C-7'), 136.3 (C-1'), 131.3 (C-4'), 130.8 (C-2, 6), 130.5 (C-3', 5'), 128.8 (C-2', 6'), 121 (C-8'), 116.3 (C-3, 5), 42.6 (C-8), 35.7 (C-7).

Paprazine (12)

White powder. EIMS $m/z(\%)$: 283(M^+ , 3), 164 (68), 147 (100), 120 (70), 107 (20), 77 (10). 1H NMR (CD_3OD , 500 MHz): δ 7.43 (1H, d, $J=15.7$ Hz, H-7'), 7.39 (2H, d, $J=8.6$ Hz, H-2', 6'), 7.05 (2H, d, $J=8.4$ Hz, H-3', 5'), 6.78 (2H, d, $J=8.6$ Hz, H-3, 5), 6.71 (2H, d, $J=8.3$ Hz, H-2, 6), 6.37 (1H, d, $J=15.7$ Hz, H-8'), 3.45 (2H, t, $J=7.3$ Hz, H-8), 2.74 (2H, t, $J=7.4$ Hz, H-7'); ^{13}C NMR (CD_3OD , 125 MHz) : δ 169.2 (C-9), 160.5 (C-4), 156.9 (C-4'), 141.8 (C-7'), 131.3 (C-1), 130.7 (C-2, 6), 130.5 (C-2', 6'), 127.8 (C-1'), 118.5 (C-8'), 116.7 (3, 5), 116.3 (3', 5'), 42.5 (C-8), 35.8 (C-7).

N-trans-Feruloyl 3'-O-methyldopamine (13)

Colorless oil. EIMS m/z (%): 337. ^1H NMR (CD_3OD , 500 MHz): δ 7.43 (1H, d, $J=15.7$ Hz, H-7'), 7.09 (1H, d, $J=1.5$ Hz, H-6'), 7.01 (1H, dd, $J=8.2, 1.5$ Hz, H-2'), 6.80 (1H, d, $J=1.6$ Hz, H-6), 6.78 (1H, d, $J=8.2$ Hz, H-3'), 6.73 (1H, d, $J=8.1$ Hz, H-3), 6.65 (1H, dd, $J=8.0, 1.6$ Hz, H-2), 5.80 (1H, d, $J=15.7$ Hz, H-8'), 3.86 (2H, s, 5'-OCH₃), 3.84 (2H, s, 5-OCH₃), , 3.48 (2H, t, $J=7.1$ Hz, H-8), 2.76 (2H, t, $J=7.3$ Hz, H-7); ^{13}C NMR (CD_3OD , 125 MHz) : δ 169.2 (C-9), 149.8 (C-5'), 149.3 (C-5), 149.0 (C-4'), 146.0 (C-4), 142.1 (C-7'), 132.0 (C-1), 128.3 (C-1'), 123.2 (C-2'), 122.3 (C-2), 118.8 (C-8'), 116.5 (C-3'), 116.2 (C-3), 113.5 (C-6), 111.6 (C-6'), 56.4 (C-5-OCH₃, C-5'-OCH₃), 42.5 (C-8), 36.2 (C-7).

Moupinamide (14)

Colorless needles. EIMS m/z (%): 314(M^+ , 10), 194 (35), 177 (100), 145 (52), 120 (30), 117 (21). ^1H NMR (CD_3OD , 500 MHz): δ 7.45 (1H, d, $J=15.7$ Hz, H-7'), 7.14 (1H, d, $J=1.2$ Hz, H-6'), 7.08 (2H, d, $J=8.4$ Hz, H-2, 6), 7.03 (1H, m, H-2), 6.81 (1H, $J=8.1$ Hz, H-3'), 6.75 (2H, $J=6.4$ Hz, H-3, 5), 6.42 (1H, $J=15.7$ Hz, H-8'), 3.90 (3H, s, 5'-OCH₃), 3.48 (2H, $J=7.2$ Hz, H-8), 2.77 (2H, $J=7.4$ Hz, H-7); ^{13}C NMR (CD_3OD , 100 MHz): δ 169.2 (C-9), 1546.9 (C-4), 150.7 (C-4'), 149.3 (C-5'), 142.1 (C-7'), 131.3 (C-1), 130.7 (C-2, 6), 128.1 (C-1'), 123.2 (C-2'), 118.6 (C-8'), 116.5 (C-3'), 116.2 (C-3, 5), 111.4 (C-6').

Dihydroconiferyl dihydro-*p*-coumarate (15)

Light yellow oil. ^1H NMR (CD_3OD , 400 MHz): δ 7.03 (2H, d, $J=8.4$ Hz, H-2', 6'), 6.73 (1H, s, H-2), 6.72 (2H, d, $J=8.0$ Hz, H-3', 5'), 6.71 (1H, s, H-5), 6.56 (1H, dd, $J=8.0, 1.6$ Hz, H-6), 4.02 (2H, t, $J=6.4$ Hz, H-9), 3.80 (3H, s, H-3- OCH_3), 2.81 (2H, t, $J=7.6$ Hz, H-7'), 2.56 (2H, t, $J=7.6$ Hz, H-8'), 2.51 (2H, t, $J=7.6$ Hz, H-7), 1.84 (2H, m, H-8); ^{13}C NMR (CD_3OD , 100 MHz) : δ 175.0 (C-9'), 156.8 (C-4'), 148.9 (C-3), 145.6 (C-4), 134.2 (C-1), 132.7 (C-1'), 130.4 (2', 6'), 121.9 (C-6), 116.3 (C-3', 5'), 116.2 (C-5), 113.0 (C-2), 65.0 (C-9), 56.4 (C-3- OCH_3), 37.3 (C-8'), 32.0 (C-7), 31.7 (C-8), 31.3 (C-7').

Dihydrosinapyl dihydro-*p*-coumarate (16)

Yellow oil. ^1H NMR (CD_3OD , 500 MHz): δ 7.06 (2H, d, $J=8.1$ Hz, H-2', 6'), 6.77 (2H, d, $J=8.1$ Hz, H-3', 5'), 6.39 (2H, s, H-2, 6), 4.11 (2H, t, $J=6.4$ Hz, H-9), 3.86 (6H, s, 3- $\text{OCH}_3, 5\text{-OCH}_3$), 2.89 (2H, t, $J=7.5$ Hz, H-7'), 2.61 (2H, t, $J=7.6$ Hz, H-8'), 2.58 (2H, t, $J=7.4$ Hz, H-7), 1.94 (2H, m, H-8); ^{13}C NMR (CD_3OD , 125MHz) : δ 173.5 (C-9'), 154.4 (C-4'), 146.9 (C-3, 5), 132.8 (C-4), 132.3 (C-1), 132.0 (C-1'), 129.3 (C-2', 6'), 115.4 (C-3', 5'), 105.0 (C-2, 6), 63.9 (C-9), 56.2 (C-3, 5- OCH_3), 36.2 (C-8'), 32.2 (C-7), 30.4 (C-8), 30.1 (C-7').

3-Isopropyl-5-acetoxycyclohexene-2-one-1 (17)

White powder. ^1H NMR (CDCl_3 , 500 MHz) δ 5.68 (1H, s, H-2), 4.32 (1H, m, H-5), 2.47 (1H, ddd, H-6a), 1.98 (1H, ddd, H-4a), 1.76 (1H, ddd, H-6b), 1.78 (3H, s, 11- CH_3), 1.75 (1H, s, H-7), 1.52 (1H, ddd, H-4b), 1.46 (3H, brs, 8- CH_3), 1.26 (3H, brs,

9- CH₃); ¹³C NMR (CDCl₃, 125 MHz) δ 182.6 (C-1), 171.9 (C-10), 112.8 (C-2), 86.8 (C-3), 66.7 (C-5), 47.3 (C-6), 45.6 (C-4), 35.9 (C-7), 30.6 (C-11), 27.0 (C-9), 26.5 (C-8).

***p*-Hydroxybenzaldehyde (18)**

White needles. ¹H NMR [CD₃OD, 500 MHz]: δ 9.65 (1H, s, CHO), 7.68 (2H, d, J= 8.8), 6.81 (2H, d, J= 8.8); ¹³C NMR [CD₃OD, 125 MHz]: 192.8 (C-1-CHO), 165.3 (C-4), 133.5 (C-2, 6), 130.2 (C-1), 116.9 (C-3, 5).

Vanillin (19)

Colorless crystal. ¹H NMR [(CD₃)₂CO, 400 MHz]: 9.64 (1H, s, CHO), 7.33 (1H, dd, J= 8.4 Hz, 1.6 Hz, H-6), , 7.32 (1H, d, J= 1.6 Hz, H-2), 6.84 (1H, d, J=8.4 Hz), 3.81 (3H, s, H-3-OCH₃); ¹³C NMR [(CD₃)₂CO, 100 MHz]: δ 192.9 (C-1-CHO), 154.7 (C-4), 149.7 (C-3), 130.7 (C-1), 128.0 (C-6), 116.3 (C-5), 111.2 (C-2), 56.4 (C-4-OCH₃).

***p*-Hydroxyphenylpropionic acid (20)**

Colorless crystal. ¹H NMR (CD₃OD, 400 MHz): δ 7.06 (2H, dt, J=8.4, 2.8, 2.0 Hz, H-2,6), 6.72 (2H, dt, J=8.4, 2.8, 2.0, H-3,5), 2.82 (2H, t, 7.6 Hz, H-2') , 2.57 (2H , t, J=7.6 Hz, H-1'); ¹³C NMR (CD₃OD, 100 MHz) : δ 177.1 (C-3'), 156.7 (C-4), 133.0 (C-1), 130.3 (C-2,6), 116.2 (C-3,5), 116.2 (C-5), 37.3 (C-8), 31.3 (C-7).

Vanillic acid (21)

White crystal. ^1H NMR [CD_3OD , 400 MHz]: 7.46 (1H, brs, H-6), 7.44 (1H, d, $J = 8.2$ Hz, H-4), 6.73 (1H, d, $J = 8.2$ Hz, H-3), 3.78 (3H, s, OMe); ^{13}C NMR [CD_3OD , 100 MHz]: δ 152.6 (C-2), 148.6 (C-5), 125.3 (C-4), 123.3 (C-1), 115.8 (C-3), 113.7 (C-6), 56.4 (OCH_3).

Protocatechuic acid (22)

White crystal. ^1H NMR [$(\text{CD}_3)_2\text{CO}$, 400 MHz]: δ 7.43 (1H, dd, $J = 2.0$ Hz, H-2), 7.40 (1H, d, $J = 7.6, 2.0$ Hz, H-6), 6.79 (1H, d, $J = 7.6$ Hz, H-5); ^{13}C NMR [$(\text{CD}_3)_2\text{CO}$, 100 MHz]: δ 170.3 (C-1-COOH), 151.5 (C-4), 146.0 (C-3), 123.9 (C-6), 123.2 (C-1), 117.7 (C-2), 115.7 (C-5).

(+)-Syringaresinol (23)

Light yellow oil. ^1H NMR [$(\text{CD}_3)_2\text{CO}$, 400 MHz]: δ 6.65 (4H, s, H-2', 2'', 6', 6''), 4.27 (2H, d, $J = 4$ Hz, H-4, 8), 4.24 (2H, m, H-4e, 8e'), 3.88 (2H, m, H-4a, 8a'), 3.84 (12H, s, 3', 3'', 4', 4''- OCH_3), 3.16 (2H, m, H-1, 5'); ^{13}C NMR [$(\text{CD}_3)_2\text{CO}$, 100 MHz]: δ 149.3 (C-3', 3'', 5', 5''), 136.5 (C-4', 4''), 132.9 (C-1', 1''), 104.4 (C-2', 2'', 6', 6''), 87.6 (C-2, 6), 72.7 (C-4, 8), 56.8 (3', 3'', 5', 5''- OCH_3), 55.3 (C-1, 5).

β -sitosterol (24) and daucosterol (25)

Obtained as colorless needles and white powder respectively, identified by co-TLC and comparison of ^1H -NMR, ^{13}C -NMR and EIMS with those of authentic samples.

Figure S1. Key HMBC (H→C) correlations for **1**

Figure S2. Major ROESY correlations for **1**

Table S1. NMR Data of compound **1** in CD₃OD (δ in ppm, J in Hz)

No.	¹ H	¹³ C	HMBC	ROESY
1		150.0		
2	6.44 (s)	99.8	C-1, 3, 4, 10, 10a	3-OMe
3		154.7		
4		137.6		
4a		128.2		
4b		114.4		
5		156.5		
6	6.32 (d, J = 2.8)	103.1	C-4b, 5, 7, 8	7-OMe
7		161.7		
8	6.37 (d, J = 2.8)	107.7	C-4b, 6, 7, 9	7-OMe
8a		144.1		
9	2.49 (s)	32.4	C-10	
10	2.49 (s)	22.7	C-8a	
10a		120.1		
3-OMe	3.68 (s)	56.3	C-3	H-2
4-OMe	3.49 (s)	62.2	C-4	
7-OMe	3.69 (s)	55.6	C-7	H-6, 8

Original spectra of compound **1**.

¹H NMR:

¹³C NMR:

^1H - ^1H COSY:

Original spectra of compound 1.

HSQC:

Original spectra of compound 1.

HMBC:

Original spectra of compound **1**.

ROESY:

Original spectra of compound 1.

HREIMS:

Original spectra of compound **1**.

EIMS:

Original spectra of compound **1**.

IR: