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TERPENOIDS AND FLAVONOIDS FROM *PSEUDOTSUGA WILSONIANA*

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Key Word Index—*Pseudotsuga wilsoniana*; Pinaceae; heartwood; terpenes; flavones; lignan.

Abstract—Four new and 27 known compounds were isolated from the heartwood of *Pseudotsuga wilsoniana*. The structures of the new compounds, 9-oxo*bis*abola-1,3,5,7*E*-tetraen-15-oic acid methyl ester, 11-hydroxy*bis*abola-1,3,5,9-tetraen-15-oic acid methyl ester, (*S*)-12-hydroxyagathic acid and 4′,5-dihydroxy-7-methoxy-6-methylflavanone, were determined by chemical and spectroscopic methods. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Pseudotsuga wilsoniana (Taiwan Douglas fir) is an endemic species in Taiwan [1]. The wood is often used in building. The chemical constituents of plants of the genus *Pseudotsuga* are rarely investigated. Previous reports [2–9] indicated that terpenes and flavones are the main constituents in the leaves, wood and root of *P. menziesii* (Douglas fir). We present herein the first report of the chemical constituents of the heartwood of *P. wilsoniana*.

RESULTS AND DISCUSSION

We isolated 31 compounds from the EtOAc-soluble part of the heartwood of *P. wilsoniana*. By analyses of the physical and spectroscopic properties (mp, [α], IR, UV, mass spectrometry, ^1H and ^{13}C NMR), 27 known compounds were readily identified as borneol (**1**) [10], epijuvabiol (**2**) [11], epijuvabione (**3**) [12], methyl atlantonate (**4**) [13], atlantolone (**5**) [14], nerolidol (**8**) [15], 6,8-cycloeudesm-4(15)-en-1-ol (**9**) [16, 17], α-cadinol (**10**) [18], *cis*-communic acid (**11**) [19], 15-*nor*-14-oxolabda-8(17),12*E*-dien-19-oic acid (**12**) [20], dehydroabietic acid (**14**) [21], pomiferin A (**15**) [22], methyl 15-hydroxydehydroabietate (**16**) [23], isopimaric acid (**17**) [24], sandaracopimaric acid (**18**) [24], chrysin (**19**) [25], pinocembrin (**20**) [26], naringenin (**21**) [27], strobopinin (**22**) [28, 29], 4′,5,7-trihydroxy-6-methylflavanone (poriol, **23**) [30], 5-hydroxy-7-methoxy-6-methylflavanone (**24**) [28, 29], meridinol (**26**) [31], 4-hydroxybenzaldehyde (**27**), vanillin (**28**), *trans*-4,4′-dihydroxy-3,3′-dimethoxystilbene (**29**) [32], β-sitosterol (**30**) and β-sitostenone (**31**) [33]. The structures of the four new compounds **6a**, **7**, **13** and **25** were determined as follows.

The molecular formula $C_{16}H_{20}O_3$ of compound **6a** was deduced from its exact mass $[M]^+$ at *m/z* 260.1418. Based on the analyses of ^1H and ^{13}C NMR spectra, the structure of **6a** was assigned as 9-oxo*bis*abola-1,3,5,7*E*-tetraen-15-oic acid. The resonances at δ 7.51 (*d*, J = 8.4 Hz) and 8.02 (*d*, J = 8.4 Hz) corresponded to the aromatic protons of a phenyl moiety having two electron-withdrawing groups on *para* positions. The signals at δ_H 3.91 (*s*) and δ_C 166.6 (*s*) corresponded to the methyl ester group. An olefinic proton and a vinyl methyl group appeared at δ_H 6.49 (*s*) and 2.51 (*s*). The resonances at δ_C 201.3 (*s*), 152.1 (*s*) and 125.8 (*d*) were ascribed to the conjugated enone moiety. The base peak at *m/z* 203, $[M-C_4H_9]^+$, was attributed to a Norrish-type I cleavage. An NOE study, i.e. irradiation of H-8 (δ 6.49) causing a 10% enhancement of the signal at δ 7.51 (H-3 or H-5), supported that **6a** had the (*E*)-configuration. Compound **6a** underwent isomerisation in part, giving **6b**, on standing in $CDCl_3$ solution. The (*Z*)-configuration in **6b** was also verified by an NOE study, i.e. irradiation of H-8 (δ 6.17) causing a 10% enhancement of the methyl group (δ 2.14) at C-7. Due to the steric effect, the β-phenyl group and the enone moiety in **6b** might not be coplanar; thus **6b** showed a UV absorption at shorter wavelength (λ_{max} 256 nm) than that of **6a** (λ_{max} 284 nm).

Compound **7** showed a characteristic IR absorption at 3431 cm^{-1} for a hydroxyl group. The NMR signals at δ_H 7.21 (*d*, J = 8.4 Hz), 7.94 (*d*, J = 8.4 Hz) and 3.88 (*s*) corresponded to a *para*-substituted benzoic acid methyl ester. The signals at δ 5.45 (*m*) and 5.54 (*d*,

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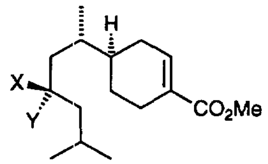
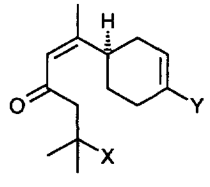
* Author to whom correspondence should be addressed.



2 X = H, Y = OH
3 X, Y = O



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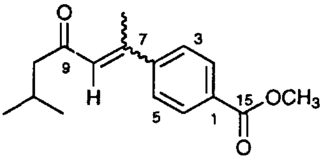
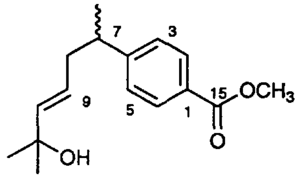
5 X = OH, Y = Me



6a (*E*)-form
6b (*Z*)-form



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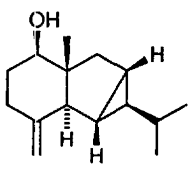

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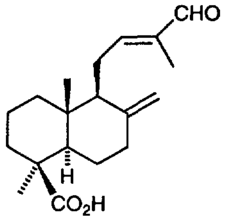

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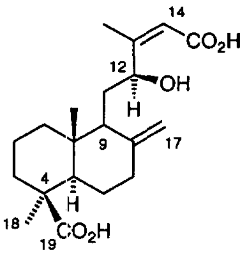

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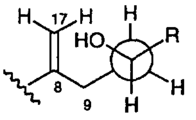
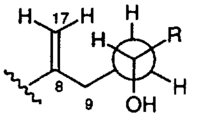


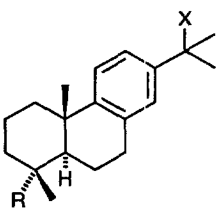
A (12*S*)



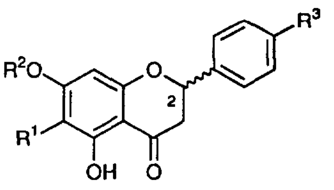
B (12*R*)

J = 15.6 Hz) were attributable to two olefinic protons with a *trans*-relationship. Compound **7** ($C_{16}H_{22}O_3$), showing the exact mass $[M]^+$ at *m/z* 262.1569, was assigned as 11-hydroxy*bis*abola-1,3,5,9-tetraen-15-oic acid methyl ester. The structure was confirmed by the ^{13}C and HMBC NMR spectra. Compound **7** exhibited an optical rotation, $[\alpha]_D$ +27.8 but the C-7 chirality is unknown.

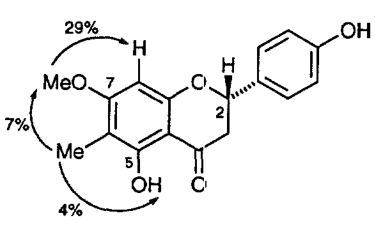
The structure of **13** was determined to be 12-hydroxyagathic acid from spectral analyses. The IR spectrum showed a strong broad absorption at 3600–2500 cm^{-1}. Two carboxyl groups appeared at δ_C 173.2 (*s*) and 183.3 (*s*) in the ^{13}C NMR spectrum. The resonances at δ_H 4.80 (*brt*) and δ_C 84.3 (*d*) corresponded to a secondary alcohol. The resonances at δ_H 4.65 (*br s*), δ_H 4.91 (*brs*), δ_C 147.2 (*s*) and δ_C 107.8 (*t*) were attributable to a 1,1-disubstituted double bond, whereas the resonances at δ_H 5.74 (*br s*), δ_C 116.7 (*d*) and δ_C 169.3 (*s*) were ascribed to a trisubstituted double bond. Irradiation of Me-13 (δ 2.06) caused an enhancement of H-14 (δ 5.74), indicating the (*Z*)-configuration. The resonances at δ_H 0.59 (*s*) and 1.23 (*s*) corresponded to two methyl groups on tertiary carbinyl centres (C-10 and C-4). The C-10 methyl group, orienting on the β-face, appeared up-field (δ 0.59) due to the shielding effect of the C-4 carboxyl group. The structure of **13** was confirmed by COSY and HMBC spectra. According to the literature [34], the C-12 chirality can be determined from the chemical shifts of the vinyl protons at C-17. Due to the deshielding effect of the hydroxyl group at C-12, the H-17 protons in the (12*S*)-isomer, presumably existing as the conformer **A**, occurred at lower fields (near δ 4.7) than the corresponding protons (near δ 4.4) in the (12*R*)-isomer, presumably existing as the conformer **B**. Compound **13**, exhibiting two H-17 protons



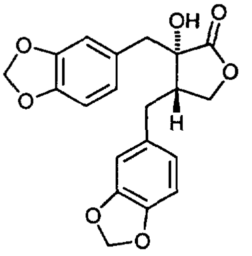
14 R = CO_2H, X = H
15 R = CH_2OH, X = H
16 R = CO_2Me, X = OH



20 (2*R*) $R^1 = R^2 = R^3 = H$
21 (2*S*) $R^1 = R^2 = H$, $R^3 = OH$
22 (2*S*) $R^1 = Me$, $R^2 = R^3 = H$
23 (2*R*) $R^1 = Me$, $R^2 = H$, $R^3 = OH$
23a (2*R*) $R^1 = R^2 = Me$, $R^3 = OH$
23b (2*R*) $R^1 = R^2 = Me$, $R^3 = OMe$
24 (2*S*) $R^1 = R^2 = Me$, $R^3 = H$



25 (2*S*)



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at δ 4.65 and 4.91, was considered to have the (12*S*)-chirality.

Compound **25** was readily recognised as a *C*-methylflavanone from its characteristic NMR resonances. Its structure was assigned as 4′,5-dihydroxy-7-methoxy-6-methylflavanone, a poriol methyl ether. The axially-oriented H-2 showed resonance at δ 5.33 (*dd*, *J* = 13, 3Hz). Two C-3 protons appeared at δ 2.75 (*dd*, *J* = 17, 3 Hz) and 3.08 (*dd*, *J* = 17, 13 Hz). The resonances at δ 6.87 (2 H, *d*, *J* = 8.5 Hz) and 7.33 (2 H, *d*, *J* = 8.5 Hz) were attributable to four protons on a *para*-disubstituted phenyl group (B-ring). Another aromatic proton, occurring at δ 6.05 as a singlet, was ascribed to H-8. Two methyl groups appeared at δ_H 1.99 (*s*, $ArCH_3$) and 3.81 (*s*, $ArOCH_3$). The C-5 hydroxyl group, hydrogen-bonded with the carbonyl group, resonated at a low-field δ 12.05. The regiochemistry of the A-ring was supported by NOE experiments. Irradiation of the C-6 methyl group (δ 1.99) caused enhancements of the C-7 methoxyl and C-5 hydroxyl groups. An enhancement of H-8 (δ 6.05) was observed on irradiation of the C-7 methoxyl group (δ 3.81). The mass spectrum showed the $[M]^+$ at *m/z* 300, a peak at *m/z* 207 $[M\text{-}C_5H_4OH]^+$ due to fragmentation of the B-ring and an intense peak at *m/z* 180 due to fragmentation of the C-ring (a retro-Diels–Alder reaction of pyranone). On treatment with diazomethane, compound **23** yielded a monoether **23a** and a *bis*ether **23b**. The monoether **23a** and compound **25** were determined to be enantiomers by spectral analyses and comparison of optical rotations. As compound **23** is known to have the (2*R*)-configuration, compound **25** should have the (2*S*)-configuration.

In summary, terpenes (**1**–**18**) and flavones (**19**–**25**) are rich in the EtOAc-soluble part of the heartwood of *P. wilsoniana*, similar to that found in Douglas fir. In addition, one lignan (**26**), two sterols (**30** and **31**) and three phenols (**27**–**29**) were isolated from this species.

EXPERIMENTAL

General

HPLC: Hibar Lichrosorb Si 60 column (10 μm, 25 cm × 1 cm i.d.). TLC: Merck silica gel 60F sheets.

Plant material

A specimen of *P. wilsoniana* Hayata is deposited in our laboratory. The wood (12–16 cm diameter), collected from mountains of central Taiwan, was air-dried (880 g) and sliced after removal of the bark. This material was exhaustively extracted with Me_2CO (7 l × 3). The combined extracts were concd to give an oil (12.8 g). The oil was partitioned between EtOAc and H_2O (1 : 1). The EtOAc-sol. part was concd (10.5 g) and subjected to silica-gel CC by elution with gradients of hexane–EtOAc Me_2CO. Appropriate frs were combined and components purified by HPLC or recrystallisation. Compounds **1** (6 mg), **2** (14 mg), **3** (16 mg), **4** (13 mg), **5** (13 mg), **6a** (7 mg), **7** (5 mg), **8** (24 mg), **9** (6 mg), **10** (7 mg), **11** (69 mg), **12** (15 mg), **13** (5 mg), **14** (46 mg), **15** (4 mg), **16** (11 mg), **17** (20 mg), **18** (18 mg), **19** (37 mg), **20** (55 mg), **21** (14 mg), **22** (14 mg), **23** (28 mg), **24** (12 mg), **25** (4 mg), **26** (38 mg), **27** (6 mg), **28** (25 mg), **29** (28 mg), **30** (20 mg) and **31** (7 mg) were obtained.

Borneol (**1**)

Solid. Mp 209–210°. $[\alpha]_D^{23}$ −35.7 (MeOH; *c* 0.8).

Epijuvabiol (**2**)

Oil. $[\alpha]_D^{23}$ +48.3 (MeOH; *c* 0.95).

Epijuvabione (**3**)

Oil. $[\alpha]_D^{23}$ +56.0 (MeOH, *c* 1.01).

Atlantonic acid methyl ester (**4**)

Oil. $[\alpha]_D^{23}$ +36.0 (MeOH, *c* 1.21).

Atlantolone (**5**)

Oil. $[\alpha]_D^{23}$ +16.5 ($CHCl_3$; *c* 0.41).

9-*Oxo*bis*abola*-1,3,5,7*E*-*tetraen*-15-*oic acid methyl ester* (**6a**)

Oil. IR ν_{max}^{neat} cm^{-1}: 1717, 1678, 1276. UV λ_{max}^{MeOH} nm (ε): 284 (26 600), 219 (10 800). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.95 (*d*, *J* = 6.6 Hz, H-12, 13), 2.18 (*m*, H-11), 2.41 (*d*, *J* = 7.0 Hz, H-10), 2.51 (*s*, H-14), 3.91 (*s*, OMe), 6.49 (*s*, H-8), 7.51 (*d*, *J* = 8.4 Hz, H-3, 5), 8.02 (*d*, *J* = 8.4 Hz, H-2, 6). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.2 (C-14), 22.7 (C-12, 13), 25.2 (C-11), 52.2 (OMe), 54.0 (C-10), 125.8 (C-8), 126.5 (C-3, 5), 129.8 (C-2, 6), 130.4 (C-1), 147.1 (C-4), 152.1 (C-7), 166.6 (C-15), 201.3 (C-9). EIMS (70 eV) *m/z* (rel. int.): 260 $[M]^+$ (16), 245 (21), 203 (100), 159 (40), 115 (40), 91 (12), 59 (21). HR-MS for $C_{16}H_{20}O_3$ requires 260.1413; found 260.1418.

9-*Oxo*bis*abola*-1,3,5,7*Z*-*tetraen*-15-*oic acid methyl ester* (**6b**)

Oil. IR ν_{max}^{neat} cm^{-1}: 1716, 1683, 1273. UV λ_{max}^{MeOH} nm (ε): 256 (11 100), 230 (11 700). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.79 (*d*, *J* = 6.4 Hz, H-12, 13), 2.02 (*m*, H-11), 2.11 (*d*, *J* = 7.2 Hz, H-10), 2.14 (*s*, H-14), 3.90 (*s*, OMe), 6.17 (*s*, H-8), 7.20 (*d*, *J* = 8.0 Hz, H-3, 5), 8.00 (*d*, *J* = 8.0 Hz, H-2, 6). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.5 (C-12, 13), 24.8 (C-11), 26.9 (C-14), 52.1 (OMe), 52.3 (C-10), 127.1 (C-3, 5), 127.4 (C-8), 129.5 (C-1), 129.6 (C-2, 6), 146.0 (C-4), 150.8 (C-7), 165.7 (C-15), 200.9 (C-9). EIMS (70 eV) *m/z* (rel. int.): 260 $[M]^+$ (21), 245 (44), 203 (100), 159 (45), 115 (33), 91 (16), 59 (28). HR-MS for $C_{16}H_{20}O_3$ requires 260.1413; found 260.1420.

11-*Hydroxy*bis*abola*-1,3,5,9-*tetraen*-15-*oic acid methyl ester* (**7**)

Oil. $[\alpha]_D^{23}$ +27.8 (MeOH; *c* 0.36). IR ν_{max}^{neat} cm^{-1}: 3431, 1714. UV λ_{max}^{MeOH} nm (ε): 240 (12 500). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.20 (*s*, Me), 1.21 (*s*, Me), 1.24 (*d*, *J* = 6.9 Hz, H-14), 2.28 (*m*, H-8), 2.81 (*m*, H-7), 3.88 (*s*, OMe), 5.45 (*m*, H-9), 5.54 (*d*, *J* = 15.6 Hz, H-10), 7.21 (*d*, *J* = 8.4 Hz, H-3, 5), 7.94 (*d*, *J* = 8.4 Hz, H-2, 6). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.1 (C-14), 29.8 (C-12, 13), 40.1 (C-7), 40.7 (C-8), 52.0 (OMe), 70.6 (C-11), 124.6 (C-9), 127.1 (C-3, 5), 128.0 (C-1), 129.7 (C-2, 6), 140.1 (C-10), 152.4 (C-4), 167.1 (C-15). EIMS (70 eV) *m/z* (rel. int.): 262 $[M]^+$ (1), 247 (6), 244 (5), 215 (26), 204 (9), 163 (100), 149 (20), 82 (58). HR-MS for $C_{16}H_{22}O_3$ requires 262.1570; found 262.1569.

Nerolidol (**8**)

Oil. $[\alpha]_D^{23}$ +16.0 ($CHCl_3$; *c* 0.4).

6,8-*Cycloeudesm*-4(15)-*en*-1-*ol* (**9**)

Solid, mp 72–73°. $[\alpha]_D^{23}$ +13.7 ($CHCl_3$; *c* 0.3).

α-*Cadinol* (**10**)

Solid. mp 74–75°. $[\alpha]_D^{23}$ −45.5 ($CHCl_3$; *c* 0.49).

Cis-Communic acid (**11**)

Oil. $[\alpha]_D^{23}$ +3.3 (MeOH; *c* 5.5).

15-Nor-14-*oxolabda*-8(17),12*E*-*dien*-19-*oic acid* (**12**)

Oil. $[\alpha]_D^{23}$ +39.5 ($CHCl_3$; *c* 0.15).

(*S*)-12-*Hydroxyagathic acid* (**13**)

Solid. mp 181–182°. $[\alpha]_D^{23}$ +57.6 (MeOH; *c* 0.21). IR ν_{max}^{KBr} cm^{-1}: 3700–2500, 3077, 1751, 1684, 1633, 1442. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.59 (*s*, H-20), 1.23 (*s*, H-18), 2.06 (*s*, H-16), 4.65 (*br s*, H-17), 4.80 (*br t*, *J* = 5.6 Hz, H-12), 4.91 (*br s*, H-17), 5.74 (*s*, H-14). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.4 (C-20), 14.7 (C-16), 19.7 (C-2), 25.9 (C-6), 27.5 (C-11), 28.9 (C-18), 37.7 (C-3), 38.5 (C-7), 39.3 (C-1), 40.7 (C-10), 44.1 (C-4), 51.8 (C-9), 56.2 (C-5), 84.3 (C-12), 107.8 (C-17), 116.7 (C-14), 147.2 (C-8), 169.3 (C-13), 173.2 (C-15), 183.3 (C-19). EIMS (70 eV) *m/z* (rel. int.): 332 $[M-H_2O]^+$ (3), 286 (2), 235 (100), 217 (12), 189 (63), 121 (40), 107 (31). HR-MS for $C_{20}H_{28}O_4$ requires 332.1988; found 332.1995.

Dehydroabietic acid (**14**)

The acid was subjected to methylation with CH_2N_2 to give the corresponding Me ester. Solid, mp 61–63°. $[\alpha]_D^{23}$ +56.8 ($CHCl_3$; *c* 0.2).

Pomiferin A (**15**)

Oil. $[\alpha]_D^{23}$ +39.6 ($CHCl_3$; *c* 0.19).

Methyl 15-*hydroxydehydrobietate* (**16**)

Solid, mp 76–78°. $[\alpha]_D^{23}$ +46.8 ($CHCl_3$; *c* 0.2).

Isopimaric acid (**17**)

Solid, mp 160–161°. $[\alpha]_D^{23}$ +1.5 ($CHCl_3$; *c* 0.7).

Sandaracopimaric acid (**18**)

Solid, mp 167–169°. $[\alpha]_D^{23}$ −18.5 ($CHCl_3$; *c* 1.2).

Chrysin (**19**)

Solid, mp 274–275°.

Pinocembrin (**20**)

Solid, mp 193–194°. $[\alpha]_D^{23}$ −47.3 (MeOH; *c* 5.48).

Naringenin (**21**)

Solid, mp 248–250°. $[\alpha]_D^{23}$ −24 (MeOH; *c* 0.15).

Strobopinin (**22**)

Solid, mp 225–228°. $[\alpha]_D^{23}$ −55.2 (MeOH: *c* 0.57).

4′5,7-*Trihydroxy*-6-*methylflavanone* (**23**)

Solid, mp 270–272°. $[\alpha]_D^{23}$ −53.8 (MeOH; *c* 0.4). Treatment of **23** (8 mg) with CH_2N_2 in Et_2O gave a monoether **23a** (2.7 mg) and a *bis*ether **23b** (3 mg), along with a recovery of **23** (1.8 mg). **23a**. Mp 91.5–92°. $[\alpha]_D^{23}$ −57.8 (MeOH; *c* 0.27). **23b**. Mp 178–178.5°. $[\alpha]_D^{23}$ −39.2 ($CHCl_3$; *c* 0.3).

5-*Hydroxy*-7-*methoxy*-6-*methylflavanone* (**24**)

Solid, mp 77–78°. $[\alpha]_D^{23}$ +45 (MeOH; *c* 0.02).

4′5-*Dihydroxy*-7-*methoxy*-6-*methylflavanone* (**25**)

Solid, mp 92–93°. $[\alpha]_D^{23}$ +74.4 (MeOH; *c* 0.03). IR ν_{max}^{KBr} cm^{-1}: 3326, 1625, 1445. UV ν_{max}^{MeOH} nm (ε): 291 (9937), 224 (shoulder, 14,444), 214 (15,348). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.99 (*s*, Me), 2.75 (*dd*, *J* = 17.3 Hz, H-3), 3.08 (*dd*, *J* = 17, 13 Hz, H-3), 3.81 (*s*, OMe), 5.33 (*dd*, *J* = 13, 3 Hz, H-2), 6.05 (*s*, H-8), 6.87 (*d*, *J* = 8.5 Hz, H-3′, 5′), 7.33 (*d*, *J* = 8.5 Hz, H-2′, 6′). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 6.9 (Me), 43.3 (C-3), 55.8 (OMe), 79.1 (C-2), 90.7 (C-8), 102.8 (C-10), 106.0 (C-6), 115.6 (C-3′, 5′), 128.0 (C-2′, 6′), 130.8 (C-1′), 156.0 (C-4′), 160.4 (C-5′), 161.2 (C-9), 165.7 (C-7), 196.0 (C-4). EIMS (70 eV) *m/z* (rel. int.): 300 $[M]^+$ (100), 299 (42), 207 (18), 194 (20), 180 (85), 152 (77), 135 (20), 120 (32). HR-MS for $C_{17}H_{16}O_5$ requires 300.0998; found 300.1000.

Meridinol (**26**)

Solid, mp 121–122°. $[\alpha]_D^{23}$ −27.3 ($CHCl_3$; *c* 0.53).

4-*Hydroxybenzaldehyde* (**27**)

Solid, mp 114–116°.

Vanillin (**28**)

Solid, mp 83–84°.

Trans-4,4′-*Dihydroxy*-3,3′-*dimethoxystilbene* (**29**)

Solid, mp 211–212°.

β-Sitosterol (**30**)

Solid, mp 136–138°. $[\alpha]_D^{23}$ −38 ($CHCl_3$; *c* 1.5).

β-Sitostenone (**31**)

Solid, mp 94–96°. $[\alpha]_D^{23}$ +79 (CHCl; *c* 1.6).

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