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Phenolic Constituents from *Dalbergia cochinchinensis*

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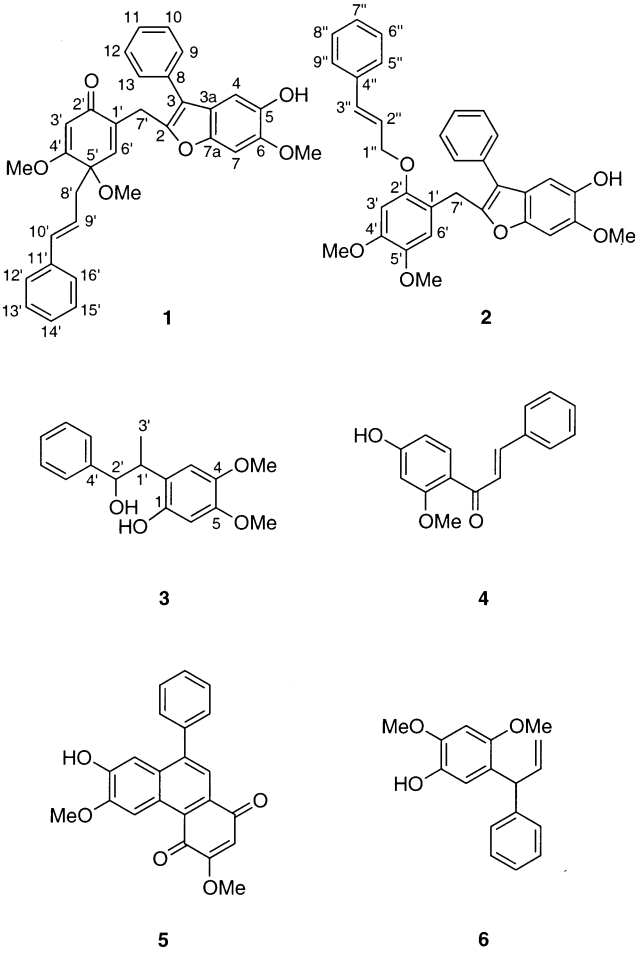
Three new phenolic compounds (**1**−**3**), along with five known phenolics, 4′-hydroxy-2′-methoxychalcone (**4**), latinone (**5**), dalbergiphenol (**6**), 7-hydroxyflavanone, and dalbergin (**7**), have been isolated from the stems of *Dalbergia cochinchinensis*. The structures of **1**−**3** were established by spectroscopic techniques including 1D and 2D NMR methods. The inhibitory activity against testosterone 5α-reductase, which causes androgen-dependent diseases, was also examined for selected compounds.

Dalbergia cochinchinensis Pierre (Leguminosae) is a perennial tree that mainly grows in Iran, Vietnam, and Indonesia. This plant has been reported to contain 10 phenolic compounds, latifolin, methoxydalbergion, 5-*O*-methyllatifolin, 2,5-dihydo-4-methoxybenzophenone, isoliquilitigenin, liquilitigenin, calycosin, 1-(2,4-dimethoxy-5-hydroxyphenyl)-1-(2-hydroxyphenyl)-1-pentene-3-ol, (2*S*)-6,7,4′-trihydroxyflavanone, and (2*S*)-6,4′-dihydroxy-7-methoxyflavanone. Of these compounds, methoxydalbergion, isoliquilitigenin, and calycosin have been reported as showing potent inhibitory activity against testosterone 5α-reductase, and latifolin and methoxydalbergion as showing potent inhibitory activity against the binding of 5α-dihydrotestosterone (DHT) to its receptor.[1] We have investigated the minor chemical constituents of the stems of this plant to obtain additional bioactive compounds and this has resulted in the isolation of four new compounds, 9-hydroxy-6,7-dimethoxydalbergiquinol, 6-hydroxy-2,7-dimethoxyneoflavene, 6,4′-dihydroxy-7-methoxyflavan, and 2,5,2′-trihydroxy-4-methoxybenzophenone, in addition to eight known compounds, including 7-hydroxy-6-methoxyflavone, which was isolated from this plant for the first time. Of these newly isolated compounds, 9-hydroxy-6,7-dimethoxydalbergiquinol and 6-hydroxy-2,7-dimethoxyneoflavene showed activity against the formation of the DHT-receptor binding complex, whereas no noticeable activity was shown against 5α-reductase.[2]

Further efforts on the chromatographic separation of this material yielded a total of eight phenolic compounds, including three new compounds (**1**−**3**). Five known compounds, 4′-hydroxy-2′-methoxychalcone (**4**), latinone (**5**), dalbergiphenol (**6**), 7-hydroxyflavanone, and dalbergin, were isolated for the first time from this plant.[3−6] Compounds were tested for their inhibitory activity against testosterone 5α-reductase.



Compound **1** was obtained as a yellow amorphous solid. This compound showed a molecular ion peak $[M]^+$ at *m*/*z* 522 in the EIMS, which was confirmed by HREIMS at *m*/*z* 522.2022, corresponding to the molecular formula $C_{33}H_{30}O_6$. The ^{1}H NMR spectrum showed 10 multiply coupled proton signals (δ_H 7.5 to 7.1) and two singlet methine proton signals (δ_H 7.10 and 6.90) in the aromatic region, as well as four olefinic proton signals (δ_H 6.30, 6.19, 5.80, and 5.72) and one exchangeable proton signal (δ_H 5.57) in the middle range. The presence of three methoxyl groups was indicated by observation of three singlet peaks at 3.87, 3.80, and 3.09 ppm, although the last resonance was shifted considerably to high field. The remaining signals were two sets of methylene protons (δ_H 3.94 and 3.87; 2.73 and 2.63). As expected from its ^{1}H NMR data, the ^{13}C NMR spectrum of

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1 showed many aromatic and/or olefinic carbons (a total of 24) along with one carbonyl (δ_C 186.2), three methoxyls (δ_C 56.4, 56.1, and 52.7), two methylenes (δ_C 42.1 and 26.4), and one quaternary carbon (δ_C 77.5) connected to an oxygen atom. The $^1H-^1H$ COSY experiment confirmed one coupling sequence among two *trans*-olefinic protons (δ_H 6.30, br d, J = 15.8 Hz; 5.80, ddd, J = 7.0, 8.2, 15.8 Hz) and one set of methylene protons (δ_H 2.73, ddd, J = 1.2, 8.2, 13.4 Hz; 2.63, ddd, J = 1.5, 7.0, 13.4 Hz) and also suggested one long-range coupled sequence among one olefinic proton (δ_H 6.19, t, J = 1.7 Hz) and another set of methylene protons (δ_H 3.94 and 3.87; each dd, J = 1.7, 17.6 Hz). Further structure elucidation of **1** was performed using an HMBC experiment, in which two sets of monosubstituted benzene rings and one tetrasubstituted benzene ring were confirmed. The third benzene ring was considered to be connected to three oxygen atoms, of which one is a hydroxyl group (δ_H 5.57s), another is a methoxyl group (δ_H 3.87), and the remaining one most likely forms an ether linkage. The proton coupling sequence among the olefinic and methylene protons, which was confirmed by the COSY experiment, was found to connect to one of the monosubstituted benzene rings to form a phenylpropenyl moiety, as HMBC long-range correlations were observed between the olefinic proton at 6.30 ppm and *ortho* aromatic carbons at 126.2 ppm and between another olefinic proton at 5.80 ppm and a quaternary aromatic carbon at 136.9 ppm. On the other hand, the *ortho* protons (δ_H 7.45, 2H) of another monosubstituted benzene ring exhibited HMBC cross-peaks with one quaternary olefinic carbon at 119.0 ppm. This quaternary carbon also showed cross-peaks with a singlet proton (δ_H 7.10) of the tetrasubstituted benzene ring and protons of another methylene (δ_H 3.94 and 3.87). Furthermore, the latter methylene protons showed HMBC correlations with olefinic carbons (δ_C 149.6, 142.5, and 138.1) and a carbonyl carbon at 186.2 ppm. One singlet olefinic proton (δ_H 5.72) showed HMBC correlations with the carbonyl carbon, two olefinic carbons (δ_C 172.9 and 138.1), and an oxygen-bonded quaternary carbon at 77.5 ppm. Another olefinic proton (δ_H 6.19) also showed similar correlations with these carbons. These HMBC correlations around the carbonyl carbon suggested a quinone system, which was quite likely a six-membered ring. The yellow color of this compound also supported the presence of the quinone system in the molecule of **1**. Two methoxyl groups present on this quinone ring were revealed by their HMBC correlations with the corresponding carbons at 77.5 and 172.9 ppm. The ROE correlations in the ROESY spectrum also supported the methoxyl group positions. The $^3J_{H,C}$ correlations between the olefinic proton (δ_H 5.80) on the phenylpropenyl moiety and one of the methoxy-linked carbons (δ_C 77.5) on the quinone ring and among the methylene protons (δ_H 2.73 and 2.63) and the olefinic carbons (δ_C 142.5 and 172.9) on them revealed that the linkage of the phenylpropenyl chain was at the methoxy-linked quaternary carbon on the quinone ring. The remaining unassigned ether linkage was expected to be between the aromatic carbon at 148.5 ppm and the olefinic carbon at 149.6 ppm to form a furan ring. These 2D NMR connectivities (Figure 1) finally established the structure of **1** as 2-[4,5-dimethoxy-5-(3-phenyl-*trans*-allyl)cyclohexa-3,6-dien-2-on-1-ylmethyl]-5-hydroxy-6-methoxy-3-phenylbenzofuran.

Compound **2** gave the same molecular ion peak as **1** and was shown to have the same molecular formula as **1** by HREIMS. The ^1H NMR spectrum of this compound showed resonances similar to **1**, which included several aromatic

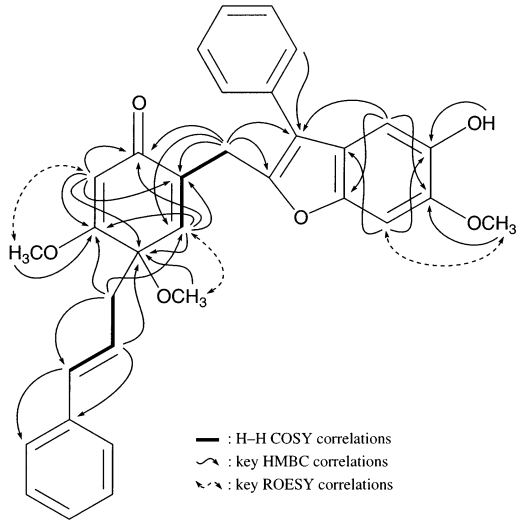

Figure 1. H−H COSY and key HMBC and ROESY correlations of **1**.

and olefinic protons, three methoxyl groups, two sets of methylenes, and one exchangeable proton. However, the chemical shifts of these signals differed from those of **1**, especially one set of methylenes which appeared as a singlet at 4.16 ppm instead of 2.73 and 2.63 ppm as in **1**. The COSY experiment confirmed only one coupling sequence among the two olefinic protons (δ_H 6.60, dt, J = 1.5, 15.9 Hz; 6.23, dt, J = 5.9, 15.9 Hz) and one equivalent methylene proton (δ_H 4.58, 2H, dd, J = 1.5, 5.9 Hz). The ^{13}C NMR spectrum of **2** did not show signals of any carbonyl carbon, downfield-shifted olefinic carbon, or oxygen-linked quaternary carbon around 77.5 ppm, which were supportive of the quinone ring in the case of **1**. Furthermore, one methylene carbon was observed at 70.6 ppm, which was shifted downfield from 42.1 ppm in **1**. The detailed structure elucidation of **2** was carried out by means of an HMBC experiment, which revealed the presence of the same benzofuran ring system as that of **1**, possessing one benzene ring at the β-position of the furan portion. Similarly, one phenylpropenyl moiety like in **1** was also apparent from the HMBC correlations. The remaining unsaturated part of the molecule of **2** was found to be a tetrasubstituted benzene ring from the HMBC analysis as follows: one singlet aromatic proton signal at 6.67 ppm had $^{2,3}J_{H,C}$ correlations with four aromatic carbon signals at 150.4, 148.3, 143.5, and 118.8 ppm; another singlet aromatic proton signal at 6.55 ppm also had similar correlations with those carbon signals; and two methoxy signals at 3.82 and 3.70 ppm each had correlations with the aromatic carbon signals at 148.3 and 143.5 ppm, respectively. The ROESY spectrum of **2** showed ROE correlations between the methoxyl signal (δ_H 3.82) and the aromatic proton signal (δ_H 6.55) and between another methoxy (δ_H 3.70) and another aromatic proton (δ_H 6.67), so that the substitution pattern of this tetrasubstituted benzene ring could be finally assigned. The connection of the benzofuran ring system to this benzene ring through one methylene unit was confirmed by the HMBC correlations of the methylene proton signal at 4.16 ppm with the aromatic carbon signals at 150.4 and 114.1 ppm. Also, the phenylpropenyl moiety was connected to the ring through an ether bond, instead of the C−C bond in **1**, and was confirmed by the HMBC correlations of the aromatic carbon at 150.4 ppm with the methylene protons (δ_H 4.58) of the oxymethylene carbon at 70.6 ppm. This spectral evidence (Figure 2) finalized the complete structure of **2** as 2-[4,5-

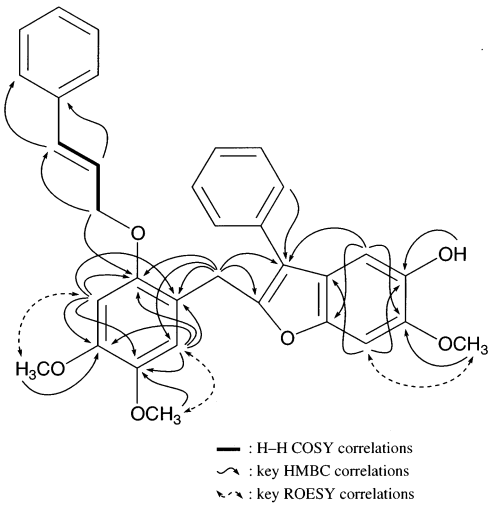

Figure 2. H−H COSY and key HMBC and ROESY correlations of **2**.

dimethoxy-2-(3-phenyl-*trans*-allyloxy)benzyl]-5-hydroxy-6-methoxy-3-phenylbenzofuran.

Compound **3** was obtained as a colorless amorphous solid and showed a molecular ion peak $[M]^+$ at *m/z* 288 in the EIMS and a quasi-molecular ion peak $[M + Na]^+$ at *m/z* 311 in the EISMS, which were confirmed by HREIMS and HRESIMS for the molecular formula $C_{17}H_{20}O_4$ and $C_{17}H_{20}O_4$-Na, respectively. The ^{1}H NMR spectrum of **3** showed signals for a monosubstituted benzene ring (δ_H 7.25, 3H; 7.08, 2H), two singlet methine protons (δ_H 6.54 and 6.14), and two methoxyl groups (δ_H 3.82 and 3.61), along with one coupling sequence consisting of a doublet methyl signal (δ_H 1.18, d, J = 7.3 Hz), a methine proton (δ_H 3.43, dq, J = 3.1, 7.3 Hz), and another methine proton (δ_H 5.07, d, J = 3.1 Hz). The ^{13}C NMR spectrum suggested the presence of two benzene rings in the downfield region. The HMBC spectrum confirmed that one of the benzene rings was tetrasubstituted, since there were correlation peaks among two methoxy protons and their linked carbons (δ_C 142.3 and 148.5) and among two singlet methine protons and quaternary aromatic carbons (δ_C 149.4, 148.5, 142.3, and 119.5). The assignment of this benzene ring was also supported by the ROESY spectrum that showed two sets of cross-peaks between the methine proton and the methoxy protons. The connectivities of these two benzene rings to the three-carbon unit, which was built up from the coupling sequence, were confirmed by the HMBC correlations of the methine proton at 5.07 ppm with the aromatic carbons at 126.7 ppm and of another methine proton at 3.43 ppm with the other aromatic ring carbons at 149.4 and 113.3 ppm. The ^{13}C NMR spectrum on addition of D_2O showed two highfield-shifted carbons (δ_C 149.406 to 149.270; δ_C 80.076 to 79.811) and suggested the presence of a phenolic hydoxyl group and a secondary hydoxyl group, respectively. These overall spectroscopic findings (Figure 3) suggested the structure of **3** as 2-(2-hydroxy-1-methyl-2-phenylethyl)-4,5-dimethoxyphenol.

Five known compounds, 4′-hydroxy-2′-methoxychalcone (**4**), latinone (**5**), dalbergiphenol (**6**), 7-hydroxyflavanone, and dalbergin, were identified on the basis of UV, IR, NMR (including 2D NMR), and MS data and by comparison with literature data.[3−6] These compounds were isolated for the first time from *D. cochinchinensis*.

Testosterone, a hormone essential for the growth of secondary male sexual characteristics, has been associated when in excess with various androgen-dependent diseases, such as prostatomegaly, prostrate cancer, male pattern baldness, hirsutism, and acne.[7,8] Testosterone is converted to 5α-dihydrotestosterone (DHT) by the enzyme 5α-reductase,[9] located in the cytoplasm of the prostate cell. DHT binds with an androgen receptor to form the DHT−receptor complex, which may result in the above-mentioned diseases.[10] To investigate the potential of the isolated compounds as antiandrogenic agents, inhibitory assays for 5α-reductase were carried out. As a result, as listed in Table 1, latinone (**5**) and dalbergiphenol (**6**) were found to show moderate and weak inhibitory activity, respectively, against 5α-reductase.

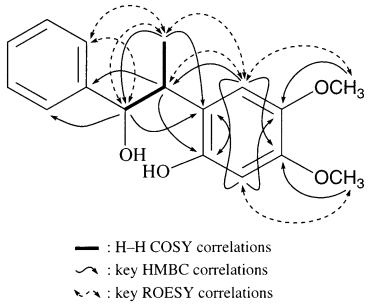

Figure 3. H−H COSY and key HMBC and ROESY correlations of **3**.

Table 1. Inhibitory Effect of Compounds[a] against Testosterone 5α-Reductase

compound	5α-reductase (inhibitory rate; %)		
	25 μg/mL	50 μg/mL	100 μg/mL
1	0.6	3.8	17.0
2	11.5	15.9	18.1
4	19.5	20.7	22.8
5	42.8	52.0	65.6
6	8.2	18.9	51.8
glycyrrhetinic acid[b]	31.7	64.7	87.1

[a] Compounds **3**, dalbergin, and 7-hydroxyflavanone were not tested. [b] Positive control.

Experimental Section

General Experimental Procedures. Melting points were determined on a Yanagimoto micro-melting point apparatus and were uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter, and values are given in 10^{-1} deg cm^2 g^{-1}. UV and IR spectra were recorded on a Hitachi U-2000 spectrophotometer and a JASCO FT/IR-5300 spectrophotometer, respectively. The one- and two-dimensional NMR spectra were recorded on Varian spectrometers (Gemini 300, Unity 400 plus, and/or Mercury 400) at 300 K using standard pulse sequences with TMS as the internal standard. Chemical shifts were reported in δ, and coupling constants (J) are given in Hz. Phase-sensitive ROESY experiments were conducted with a mixing time of 300 ms. EIMS were obtained using a Hitachi M80 spectrometer, and HREIMS spectra were measured on a VG Autospec spectrometer. ESIMS and HRESIMS were obtained using a JEOL AccuTOF spectrometer. Open column chromatography was performed on silica gel 60 (Merck). Medium-pressure liquid chromatography (MPLC) was performed with Ultra Pack (26 mm i.d. × 300 mm or 50 mm i.d. × 300 mm; Yamazen Co., Osaka, Japan) packed with 40 μm Si gel and/or 50 μm ODS. HPLC was performed with an Inertsil PREP-ODS column (5 mm i.d. × 250 mm for analytical work, 20 mm i.d. × 250 mm for preparative work; GL Science Inc., Tokyo, Japan) packed with 10 μm ODS. TLC was performed on precoated Merck silica gel 60 F_{254} or Merck RP-18 F_{254}, and spots were visualized by heating with 10% H_2SO_4 and/or by UV light at 254 nm.

Plant Material. The stems of *Dalbergia cochinchinensis* were collected from a northern region of Vietnam (around Ha

Noi) in the summer of 1993. The plant material was air-dried, and voucher specimens have been deposited at the National Institute of Health Sciences, Tokyo Japan, and at the Biological Science Research Center, Lion Corporation, Japan.

Extraction and Isolation. The dried stems (1.5 kg) of *D. cochinchinensis* were extracted with hot EtOH, and evaporation in vacuo gave 172 g of an EtOH extract, which was then fractionated by silica gel (1 kg, Merck 60−120 mesh) open column chromatography by gradient elution with *n*-hexane−EtOAc and EtOAc−MeOH mixtures. The fractions eluted by *n*-hexane−EtOAc (8:2) contained compounds **1**, **2**, **5**, **6**, and dalbergin, whereas the fractions eluted with *n*-hexane−EtOAc (7:3) contained compounds **3**, **4**, and 7-hydroxyflavanone. Further separation of the fractions by MPLC on silica gel (CH_2Cl_2−EtOAc) and/or ODS (MeOH−water) and successive purification by HPLC on an ODS column using acetonitrile−water solvent systems finally resulted in the purification of eight compounds, namely, **1** (25 mg), **2** (18 mg), **3** (17 mg), **4** (20 mg), **5** (21 mg), **6** (111 mg), 7-hydroxyflavanone (19 mg), and dalbergin (36 mg).

Compound 1: yellow amorphous solid; mp 78−83 °C; $[\alpha]^{25}_D$ +23.6° (*c* 0.44, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 237 (4.47), 293 (4.06), 375 (3.61) nm; IR (KBr) ν_{max} 3422, 1609, 1485, 1443, 1370, 1321, 1219, 1155, 1086, 970, 851, 750, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (2H, m, H-9, 13), 7.35 (2H, m, H-10, 12), 7.29 (1H, m, H-11), 7.22 (2H, m, H-13′, 15′), 7.20 (1H, m, H-14′), 7.13 (2H, m, H-12′, 16′), 7.10 (1H, s, H-4), 6.90 (1H, s, H-7), 6.30 (1H, br d, J = 15.8 Hz, H-10′), 6.19 (1H, t, J = 1.7 Hz, H-6′), 5.80 (1H, ddd, J = 7.0, 8.2, 15.8 Hz, H-9′), 5.72 (1H, s, H-3′), 5.57 (br s, O*H*-5), 3.94 (1H, dd, J = 1.7, 17.6 Hz, H-7′a), 3.87 (3H, s, OCH_3-6), 3.87 (1H, dd, J = 1.7, 17.6 Hz, H-7′b), 3.80 (3H, s, OCH_3-4′), 3.09 (3H, s, OCH_3-5′), 2.73 (1H, ddd, J = 1.2, 8.2, 13.4 Hz, H-8′a), 2.63 (ddd, J = 1.5, 7.0, 13.4 Hz, H-8′b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.2 (C, C-2′), 172.9 (C, C-4′), 149.6 (C, C-2), 148.5 (C, C-7a), 145.0 (C, C-6), 142.7 (C, C-5), 142.5 (CH, C-6′), 138.1 (C, C-1′), 136.9 (C, C-11′), 134.3 (CH, C-10′), 132.4 (C, C-8), 128.8 (2 × CH, C-10, 12), 128.5 (2 × CH, C-9, 13 or C-13′, 15′), 128.4 (2 × CH, C-13′, 15′ or C-9, 13), 127.4 (CH, C-14′), 127.2 (CH, C-11), 126.2 (2 × CH, C-12′, 16′), 122.2 (CH, C-9′), 121.1 (C, C-3a), 119.0 (C, C-3), 104.8 (CH, C-3′), 103.8 (CH, C-4), 94.5 (CH, C-7), 77.5 (C, C-5′), 56.4 (CH_3, 6-OCH_3), 56.1 (CH_3, OCH_3-4′), 52.7 (CH_3, OCH_3-5′), 42.1 (CH_2, C-8′), 26.4 (CH_2, C-7′); EIMS *m*/*z* 522 [M^+] (22), 405 (100), 356 (38), 240 (82), 225 (37), 167 (19), 117 (76), 91 (23); HREIMS *m*/*z* 522.2022 [M^+] (calcd for $C_{33}H_{30}O_6$, 522.2042).

Compound 2: amorphous solid; mp 63−68 °C; UV (MeOH) λ_{max} (log ϵ) 237 (4.27), 285 (4.08) nm; IR (KBr) ν_{max} 3430, 1607, 1512, 1449, 1318, 1200, 1158, 1019, 860, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50 (2H, m, H-9, 13), 7.38 (2H, m, H-10, 12), 7.28 (5H, m, H-11, 12′, 13′, 15′, 16′), 7.22 (1H, m, H-11′), 7.08 (1H, s, H-4), 6.94 (1H, s, H-7), 6.67 (1H, s, H-6′), 6.60 (1H, dt, J = 1.5, 15.9 Hz, H-3″), 6.55 (1H, s, H-3′), 6.23 (1H, dt, J = 5.9, 15.9 Hz, H-2″), 5.46 (br s, O*H*-5), 4.58 (2H, dd, J = 1.5, 5.9 Hz, H-1″), 4.16 (1H, s, H-7′), 3.87 (3H, s, OCH_3-6), 3.82 (3H, s, OCH_3-4′), 3.70 (3H, s, OCH_3-5′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0 (C, C-2), 150.3 (C, C-2′), 148.3 (2 × C, C-7a, 4′), 144.8 (C, C-6), 143.5 (C, C-5′), 142.6 (C, C-5), 136.5 (C, C-4″), 132.9 (C, C-8), 132.7 (CH, C-2″), 128.9 (2 × CH, C-9, 13), 128.7 (2 × CH, C-10, 12), 128.6 (2 × CH, C-6″, 8″), 127.8 (CH, C-7″), 127.0 (CH, C-11), 126.6 (2 × CH, C-5″, 9″), 124.9 (CH, C-2″), 121.4 (C, C-3a), 118.8 (C, C-1′), 117.8 (C, C-3), 114.1 (CH, C-6′), 103.7 (CH, C-4), 99.8 (CH, C-3′), 94.6 (C, C-7), 70.6 (CH_2, C-1″), 56.6 (CH_3, OCH_3-5′), 56.4 (CH_3, OCH_3-6), 56.2 (CH_3, OCH_3-4′), 26.9 (CH_2, C-7′); EIMS *m*/*z* 522 [M^+] (15), 405 (100), 356 (37), 240 (45), 225 (22), 167 (23), 117 (94), 91 (23); HREIMS *m*/*z* 522.2019 [M^+] (calcd for $C_{33}H_{30}O_6$, 522.2042).

Compound 3: amorphous solid; mp 37−45 °C; $[\alpha]^{25}_D$ −44.9° (*c* 0.25, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224 (4.03), 290 (3.76) nm; IR (KBr) ν_{max} 3442, 1620, 1512, 1451, 1202, 1028 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.25 (3H, m, H-6′, 7′, 8′), 7.08 (2H, m, H-5′, 9′), 6.54 (1H, s, H-6), 6.14 (1H, s, H-3), 5.07 (1H, d, J = 3.1 Hz, H-2′), 3.82 (3H, s, 5-OCH_3), 3.61 (3H, s, 4-OCH_3), 3.43 (1H, dq, J = 3.1, 7.3 Hz, H-1′), 1.18 (3H, d, J = 7.3 Hz, H-3′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.4 (C, C-1), 148.5 (C, C-5), 142.3 (C, C-4), 140.5 (C, C-4′), 127.9 (3 × CH, C-6′, 7′, 8′), 126.7 (2 × CH, C-5′, 9′), 119.5 (C, C-2), 113.3 (CH, C-3), 102.1 (CH, C-6), 80.1 (CH, C-2′), 56.6 (CH_3, OCH_3-4), 55.8 (CH_3, OCH_3-5), 41.1 (CH, C-1′), 14.1 (CH_3, C-3′); EIMS *m*/*z* 288 [M^+] (18), 270 (3), 181 (100), 161 (12), 77 (19); HREIMS *m*/*z* 288.1370 [M^+] (calcd for $C_{17}H_{18}O_3$, 288.1362); ESI+ *m*/*z* 599 [2M + Na^+] (13), 311 [M + Na^+] (74), 271 [M − H_2O + H^+] (100); HREIMS *m*/*z* 311.1258 [M + Na^+] (calcd for $C_{17}H_{20}NaO_4$, 311.1259).

5α-Reductase Inhibition Assay. The isolated compounds were examined for their inhibitory activities against 5α-reductase in the same manner as previously reported.[1]

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