Secondary Metabolites from the Wood Bark of *Durio zibethinus* and *Durio kutejensis*

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Phytochemical exploration of a wood bark extract from *Durio zibethinus* afforded two new triterpenoids, namely, methyl 27-*O*-*trans*-caffeoylcylicodiscate (**1**) and methyl 27-*O*-*cis*-caffeoylcylicodiscate (**2**), a new phenolic, 1,2-diarylpropane-3-ol (**3**), and seven known compounds, fraxidin, eucryphin, boehmenan, *threo*-carolignan E, (−)-(3*R*,4*S*)-4-hydroxymellein, methyl protocatechuate, and (+)-(*R*)-de-*O*-methyllasiodiplodin (**4**). In addition, chemical analysis of a wood bark extract from *Durio kutejensis* yielded the new triterpenes 3*β*-*O*-*trans*-caffeoyl-2α-hydroxyolean-12-en-28-oic acid (**5**) and 3*β*-*O*-*trans*-caffeoyl-2α-hydroxytaraxest-12-en-28-oic acid (**6**) together with four known compounds, maslinic acid, arjunolic acid, 2,6-dimethoxy-*p*-benzoquinone, and fraxidin. The structures of all compounds were determined on the basis of spectroscopic data.

Trees of the genus *Durio*, belonging to the Bombacaceae family, produce durian, one of the most popular and famous seasonal fruits in Southeast Asia, and have been cultivated for centuries in tropical regions. The popular names for this fruit are durian (Indonesia), duran (Philippines), du-yin (Myanmar), thu-reen (Cambodia), thourien (Laos), thurian (Thailand), duren (Malaysia), and saurieng (Vietnam).[1] The genus has 28 species, 19 of which are found in Borneo and 8 of which produce edible fruit. Traditionally, some parts of this plant have biological activity. For example, the seeds are believed to possess a toxic property that causes shortness of breath, the juice from durian leaves and roots is therapeutic as a treatment for fever, and the ash of burned rind is taken after childbirth.[2] There is little information about secondary metabolites from *Durio*. Previous studies on the chemical composition of durian fruit investigated volatile sulfur constituents,[3] α-tocopherol,[4] and polysaccharides.[5] In this paper we report the isolation and structure identification of some chemical constituents of two species of *Durio*, namely, *Durio zibethinus* Murr and *Durio kutejensis* (Hassk.) Becc.

The ethyl acetate-soluble components of a methanol extract of wood bark from *D. zibethinus* were fractionated by silica flash chromatography followed by C_{18} HPLC. Two new triterpenoids, methyl 27-*O*-*trans*-caffeoylcylicodiscate (**1**) and its isomer methyl 27-*O*-*cis*-caffeoylcylicodiscate (**2**), and a new phenolic acid, (−)-1-(4′-hydroxy-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)propan-3-ol (**3**), were isolated together with seven known compounds, fraxidin,[6] eucryphin,[7,8] boehmenan,[9,10] *threo*-carolignan E,[9,10] (−)-(3*R*,4*S*)-4-hydroxymellein,[11] methyl protocatechuate,[12] and (+)-(*R*)-de-*O*-methyllasiodiplodin (**4**).[13] From the chloroform-soluble components of a methanol extract of the wood bark of *D. kutejensis*, we isolated two other new triterpenes, 3*β*-*O*-*trans*-caffeoyl-2α-hydroxyolean-12-en-28-oic acid (**5**) and 3*β*-*O*-*trans*-caffeoyl-2α-hydroxytaraxest-12-en-28-oic acid (**6**), together with the known compounds maslinic acid,[14,15] arjunolic acid,[16] 2,6-dimethoxy-*p*-benzoquinone,[17] and fraxidin.[6] The structures of these compounds were solved by MS and NMR methods (^{1}H, ^{13}C, DEPT135, HSQC, HMBC, DQF-COSY, NOESY, and HSQC-TOCSY).

Compound **1** was obtained as a white, amorphous solid from *D. zibethinus*. The positive-ion HRESIMS of **1** exhibited a pseudomolecular ion at *m*/*z* 671.3903 [M + Na]$^+$, corresponding to the formula $C_{40}H_{56}O_7$. The ^{1}H NMR spectrum showed four tertiary methyl groups at *δ* 0.92, 0.74, 0.89, and 1.00 (CH_3-23, CH_3-24, CH_3-25, CH_3-26, respectively), a terminal methylene group at *δ* 4.74 and 4.62 (H-29a/H-29b), and an allylic methyl signal at *δ* 1.72 (s, CH_3-30). An oxymethine proton was observed at *δ* 3.13 (dd, *J* = 5.0, 11.3 Hz, H-3), and its configuration was deduced by the NOESY cross-peak correlation from *δ* 3.13 to *δ* 0.77 (1H, m, H-5). Two doublets at *δ* 4.66 (1H, *J* = 12.9 Hz, H-27a) and 4.50 (1H, *J* = 12.9 Hz, H-27b) were assigned to the methylene protons of a primary alcohol group, while a singlet at *δ* 3.66 indicated a −OMe group. These signals were typical of a 3*β*-lupane triterpene skeleton and corresponded to the methyl ester of a substituted cylicodiscic acid.[18] The presence of a caffeoyl group[19] was deduced by *trans* olefinic protons at *δ* 6.23 (H-8′) and 7.52 (H-7′) with a large coupling constant (*J* = 15.8 Hz) and by a 1,3,4-trisubstituted benzene ring at *δ* 6.77 (d, *J* = 8.2 Hz, H-5′), 7.02 (d, *J* = 2.0 Hz, H-2′), and 6.93 (dd, *J* = 2.0, 8.2 Hz, H-6′). There were two carbonyl signals at *δ* 178.1 (C-28) and 169.4 (C-9′) from ^{13}C NMR.

The location of the caffeoyl group at C-27 (*δ* 64.2) was established by the long-range correlations from the geminal protons at *δ* 4.50 and 4.66 to the carbonyl signals at *δ* 169.4, and to C-8, C-13, and C-15 (*δ* 42.7, 40.4, and 25.2, respectively). The two olefinic protons at *δ* 6.23 and 7.52 exhibited correlations with the same ester carbonyl. The HMBC spectrum also showed correlations from the geminal protons at *δ* 1.32 (m, H-16b) and 2.25 (m, H-16a) (δ_C 33.5), the methine proton at *δ* 1.82 (m, H-18), and the methoxy signal to the carbonyl at *δ* 178.1, assigned to C-28. Therefore, compound **1** was identified as a new compound, methyl 27-*O*-*trans*-caffeoylcylicodiscate. A *trans*-*p*-coumaroyl ester of cylicodiscic acid has previously been reported.[20]

Compound **2** was obtained as a white, amorphous solid, and the molecular formula was deduced as $C_{40}H_{56}O_7$ from HRESIMS data. During chromatographic separation, it appeared that compound **2** was interconverting with **1**; consequently, identification of **2** was achieved by comparison with the data for **1**. The ^{1}H spectrum of **2** was very similar to **1** except for the appearance of a proton signal at *δ* 4.36 (1H, d, *J* = 12.6 Hz, H-27b) instead of *δ* 4.50, while the *meta* proton in the 1,3,4-trisubstituted benzene ring appeared at *δ* 7.23 (d, *J* = 2.1 Hz, H-2′) due to the anisotropic effect of the carbonyl group. Furthermore, the appearance of two olefinic protons at *δ* 5.75 (H-8′) and 6.81 (H-7′) with a coupling constant of 12.6 Hz was consistent with a *cis* configuration. Therefore, compound **2** was assigned as methyl 27-*O*-*cis*-caffeoylcylicodiscate. The ^{13}C signals for the *cis* phenylpropanoid moiety were assigned by HSQC and HMBC correlations, while the triterpene ^{13}C signals were indistinguishable from those shown by compound **1**.

Compound **3** was isolated as a white, amorphous solid. HRESIMS indicated that it had a molecular formula of $C_{17}H_{20}O_5$. ^{1}H NMR

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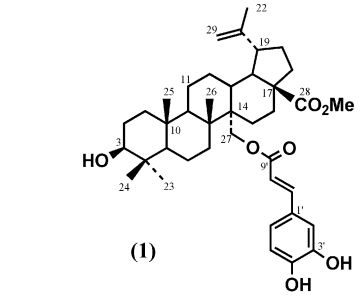

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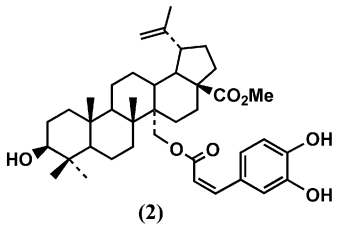

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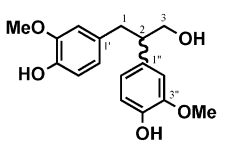

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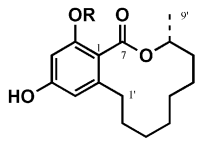

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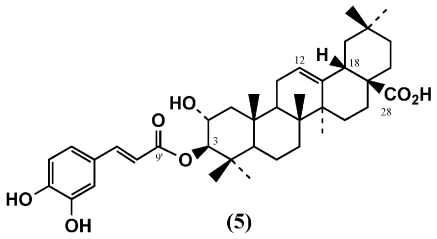
(8) R = CH_3



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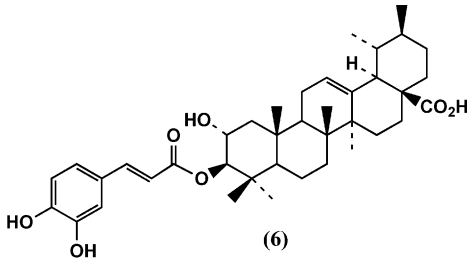

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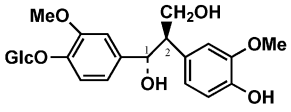

(7)

showed signals for a methylene group at δ 2.67 (1H, dd, J = 9.0, 13.5 Hz, H-1b) and 2.97 (1H, dd, J = 5.5, 13.5 Hz, H-1a) and a methine at δ 2.85 (1H, m, H-2), which were linked by COSY data. Two protons for a primary alcohol at δ 3.70 (d, J = 6.5 Hz, CH_2-3) were COSY correlated to H-2. The presence of two 1,3,4-trisubstituted benzene rings was determined from the characteristic ^{1}H NMR data at δ 6.62 (1H, d, J = 2.0 Hz, H-2″), 6.68 (1H, d, J = 8.3 Hz, H-5″), 6.58 (1H, dd, J = 2.0, 8.3 Hz, H-6″) and at δ 6.46 (1H, br s, H-2′), 6.60 (1H, d, J = 8.5 Hz, H-5′), 6.47 (1H, dd, J = 1.9, 8.5 Hz, H-6′). Two signals at δ 3.67 and 3.76 were typical of methoxy groups.

A phenylpropanoid moiety was constructed by long-range correlations from H-1a/H-1b at δ 2.97 and 2.67 to C-2′, C-6′, and C-3 at δ 114.1, 122.7, and 67.0, respectively, and from H-2 to C-1′ at δ 133.3. The second 1,3,4-trisubstituted aromatic system was attached to C-2 since there were long-range correlations from the two aromatic protons H-2′ at δ 6.62 and H-6′ at δ 6.58 to the C-2 signal at δ 51.7. Additional correlations were from the two sets of methylene protons CH_2-1 and CH_2-3 to the quaternary aromatic carbon C-1″ at δ 135.5. The two methoxy groups at δ 3.67 and 3.76 were linked to C-3′ and C-3″. Therefore, this new compound was assigned as (−)-1-(4′-hydroxy-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)propan-3-ol. This type of compound has previously been found as a product of lignin degradation,[21,22] while (1*S*,2*R*)-1-(4′-*O*-β-D-glucopyranosyl-3′-methoxyphenyl)-2-(4″-hydroxy-3″-methoxyphenyl)-1,3-propanediol (**7**) has been isolated from *Symplocos caudata* Wall.[23] There was insufficient compound to determine the absolute stereochemistry of **3** by chemical correlation to **7**.

We also evaluated the ^{13}C NMR data for (+)-(*R*)-de-*O*-methyllasiodiplodin using HSQC-TOCSY sequence data, starting from the ^{1}H NMR signals for H-8′ at δ 5.14 (m), for H-1′ [δ 2.47 (m, H-1′b); 3.25 (m, H-1′a)], and for H-7′ [δ 1.76 (m, H-7′b); 1.90 (m, H-7′a)]. In the HSQC-TOCSY spectrum, H-8′ showed correlations to signals at δ 20.1, 31.0, and 24.6, assigned to C-9′, C-7′, and C-6′ respectively. Protons H-7′a and H-7′b showed correlations to C-6′, C-8′, and C-9′. The methylene CH_2-1′ showed correlations to δ 30.7 and 27.2, assigned to C-2′ and C-3′, respectively. One of the methylene protons attached to C-3′ showed a correlation to C-2′, and to a signal at δ 21.1, assigned to C-4′. The remaining carbon at δ 24.1, assigned to C-5′, showed correlations from the two H-6′ protons. The absolute configurations of the (+)-isomer of lasiodiplodin (**8**) and its de-*O*-methyl compound **4** are frequently represented as *S* in the literature;[24] however asymmetric syntheses of **4** and **8** clearly indicate that the natural (+)-isomer has the *R* configuration.[25]

The chemistry of *D. kutejensis* was then explored. Compound **5** was isolated as a yellowish amorphous solid of molecular formula $C_{39}H_{54}O_7$ by HRESIMS. The ^{1}H NMR spectrum revealed the presence of seven methyl singlets at δ 1.18, 1.05, 0.90, 0.89, and 0.84 (CH_3-27, CH_3-25, CH_3-29, CH_3-23, and CH_3-26, respectively) and at δ 0.94 (6H, s, CH_3-24 and CH_3-30). In addition, there were two oxymethine protons at δ 4.60 (d, J = 9.5 Hz, H-3α) and 3.83 (ddd, J = 4.4, 9.5, 11.7 Hz, H-2β), one olefinic proton signal at δ 5.25 (t, J = 3.4 Hz, H-12), and a methine proton at δ 2.86 (dd, J = 3.0, 13.5 Hz, H-18). These signals suggested **5** to be an oleanane-type triterpene and corresponded to the maslinic acid skeleton.[14,15] A *trans*-caffeoyl moiety was indicated by the alkene signals at δ 6.31 and 7.55, together with signals for a 1,3,4-trisubstituted benzene ring at δ 7.04, 6.94, and 6.77. The caffeoyl group attached at C-3 (δ 85.4) was confirmed by long-range correlations from H-3, H-8′, and H-7′ with C-9′ at δ 169.5. A second carbonyl group (δ_C 182.5; C-28) showed HMBC correlations from H-18 and from a methylene proton at δ 1.74 (H-22a). Therefore, compound **5** was assigned as a new compound, 3β-*O*-*trans*-caffeoyl-2α-hydroxy-olean-12-en-28-oic acid.

Compound **6** was obtained as a white, amorphous powder. HRESIMS indicated that the isolated compound had a molecular formula of $C_{39}H_{54}O_7$. ^{13}C NMR and DEPT135 indicated that compound **6** had seven methyls, eight methylenes, 13 methines, and 11 quaternary carbons including two carbonyls at δ 169.6 (C-9′) and 182.4 (C-28). The ^{1}H NMR spectrum of **6** was similar to that of **5**, except for the presence of two methyl doublets [δ 0.95 (CH_3-29) and 0.88 (CH_3-30)] and five methyl singlets [δ 1.14, 1.07, 0.94, 0.89, and 0.87 (CH_3-27, CH_3-25, CH_3-24, CH_3-23, and CH_3-26, respectively)] instead of seven methyl singlets. Moreover, the H-18 signal was changed in appearance from δ 2.86 (dd, J = 3.0, 13.5 Hz) in **5** to δ 2.22 (d, J = 11.3 Hz) in **6**, with a *trans*-diaxial relationship to H-19 at δ 1.37. All these signals indicated a 3β-taraxest-12-ene triterpene skeleton.[26,27] A *trans*-caffeoyl group, recognized by comparison with **5**, was located at C-3 since there were HMBC correlations from an oxygenated proton at δ 4.62 (d,

J = 10 Hz, H-3) and the two olefinic protons at δ 7.55 (d, J = 15.8 Hz, H-7′) and 6.31 (d, J = 15.8 Hz, H-8′) to the ester carbonyl C-9′. Furthermore, the HMBC spectrum also showed correlations between H-18 and from a methylene proton at δ 1.63 (m, H-22b) to the carbonyl at C-28. Hence, compound **6** was deduced as the new triterpene 3β-*O*-*trans*-caffeoyl-2α-hydroxytaraxest-12-en-28-oic acid.

The isolation of the new triterpene acids **5** and **6**, together with maslinic acid and arjunolic acid, from *D. kutejensis* contrasts with the triterpene methyl esters **1** and **2** that were obtained from *D. zibethinus*. A careful search using LC-MS of other fractions of *D. zibethinus* did not reveal the presence of triterpene carboxylic acids despite the identical isolation methods used for the two species. Therefore, we inferred that the methyl esters **1** and **2** were natural products.

The known compounds isolated from the two species were identified on the basis of 2D NMR data and comparison of the NMR data with published data,[6−17] and by preparation of (−)-(3*R*,4*S*)-4-hydroxymellein diacetate.[11]

In conclusion, a range of oxygenated secondary metabolites, including triterpenoids, phenylpropanoids, polyketides, and shikimate compounds, have been isolated from the two *Durio* species. On the basis of this information, the phenylpropanoid moiety may represent typical chemistry for the *Durio* genus. Polyketides such as (−)-(3*R*,4*S*)-4-hydroxymellein and (+)-**4** are products characteristic of fungi and lead us to speculate that fungi may have been growing on the bark that was sampled.[24]

Experimental Section

General Experimental Procedures. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Optical rotations were measured on Perkin-Elmer 241-MC and Jasco P-1010 polarimeters. HREIMS were recorded on a Finnigan Mat 900 XL-Trap, and HRESIMS were measured on a Kratos MS25RFA instrument. The ^{1}H, HSQC, HMBC, DQF-COSY, and NOESY data were observed on a Bruker Avance 500 MHz spectrometer, while HSQC-TOCSY data were acquired on a Bruker Avance 750 MHz spectrometer. ^{13}C NMR and DEPT135 data were recorded using Bruker Avance 400, 500, or 750 MHz spectrometers. ^{1}H spectra were referenced relative to either MeOH-d_4 (δ = 3.30 ppm) or $CDCl_3$ (δ = 7.24 ppm), and ^{13}C spectra were referenced relative to either MeOH-d_4 (δ = 49.0 ppm) or $CDCl_3$ (δ = 77.0 ppm). Flash column chromatography (FC) was carried out on silica gel 60 (230−400 mesh). Thin-layer chromatography (TLC) analysis was performed on precoated silica gel plates (Kieselgel 60 F_{254} or RP-18 F_{254s}, 20 × 20 cm, 0.25 mm thick, Merck). Spots were detected under UV light at 254 and 366 nm or by using ceric sulfate spray reagent. RP-HPLC was performed on an Agilent 1100 series instrument with a variable-wavelength UV detector. Semipreparative separation used a μBondapak C_{18} (7.8 × 300 mm) 10 μm column. All solvents used were distilled prior to use.

Plant Material. Samples of the wood bark from *Durio zibethinus* Murr and from *Durio kutejensis* (Hassk.) Becc. were collected in Pontianak, West Borneo, Indonesia, in May 2004. The plants were identified by the staff at the Herbarium Bogoriense, Bogor Botanical Garden, Bogor, Indonesia, and the voucher specimens (#358 for *D. zibethinus*; #019 for *D. kutejensis*) have been deposited at the herbarium.

Extraction and Isolation. Powdered wood bark (3 kg) of *D. zibethinus* Murr was macerated exhaustively with MeOH. The MeOH extract, on removal of solvent under reduced pressure, gave a dark brown residue (50 g, 1.7%). This residue was solubilized in a mixture of MeOH−H_2O (20%) and partitioned between *n*-hexane and EtOAc. The ethyl acetate extract (16.3 g) was fractionated by NP flash column chromatography using *n*-hexane, EtOAc, and MeOH in increasing polarity. Thirteen fractions (Z1−Z13) were ultimately obtained on combining the eluates on the basis of TLC. Fraction Z4 (350 mg) was further chromatographed by Si gel flash column chromatography using *n*-hexane and EtOAc in order of increasing polarity to yield eight fractions (Z4a−Z4h). Fractions Z4e and Z4f were combined and then subjected to repeated NP flash column chromatography, followed by purification with preparative C_{18}-HPLC (70−80% AcCN−H_2O gradient over 40 min, flow rate 1.3 mL/min, UV detection at λ 254 nm) to afford **1** (2 mg) and **2** (1.2 mg). Compound **3** (0. 6 mg) was isolated from fraction Z8 (940 mg) by repeated flash column chromatography using *n*-hexane, $CHCl_3$, and MeOH in order of increasing polarity, followed by purification using RP-HPLC (10−30% AcCN−H_2O gradient over 40 min then 30−100% AcCN−H_2O over 20 min, flow rate 1.3 mL/min, UV detection at λ 254 nm). Repeated flash column chromatography of the combined fractions Z1, Z3, Z8, and Z12 on silica gel and further purification by semipreparative C_{18}-HPLC afforded fraxidin (6 mg), eucryphin (7 mg), boehmenan (8 mg), *threo*-carolignan E (5 mg), (−)-(3*R*,4*S*)-4-hydroxymellein (5 mg), methyl protocatechuate (8 mg), and (+)-(*R*)-de-*O*-methyllasiodiplodin **4** (5.5 mg).

Wood bark (3 kg) of *D. kutejensis* (Hassk.) Becc. was macerated with methanol for 3 days, providing 30 g of residue (1%), which was then partitioned using *n*-hexane, chloroform, and EtOAc, respectively. The chloroform extract (6.80 g) was chromatographed using *n*-hexane, chloroform, and methanol by increasing polarity and gave nine fractions (KC1−KC9). Fraction KC6 (3.04 g) was further fractionated by flash column chromatography to obtain 11 fractions (KC6A−KC6K). Fractions KC6E and KC6F were combined and further purified by preparative C_{18}-HPLC (85% MeOH−H_2O isocratic over 60 min, 2 columns in series, flow rate 1.5 mL/min, UV detection at λ 254 nm) to afford **5** (3 mg). Fraction KC6H (276 mg) was also chromatographed by flash column and purified with C_{18}-HPLC (85% MeOH−H_2O isocratic over 30 min, flow rate 1.5 mL/min, UV detection at λ 254 nm) to yield **6** (6.5 mg). Further repeated flash column chromatography of the fractions KC3, KC4, KC5, and KC6K on silica gel and purification by semipreparative C_{18}-HPLC afforded 2,6-dimethoxy-*p*-benzoquinone (1.7 mg), fraxidin (3.2 mg), maslinic acid (6.9 mg), and arjunolic acid (0.9 mg).

Compound 1: white, amorphous solid; $[\alpha]^{24}_D$ −104.4 (*c* 0.09, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.52 (1H, d, J = 15.8 Hz, H-7′), 7.02 (1H, d, J = 2.0 Hz, H-2′), 6.93 (1H, dd, J = 2.0, 8.2 Hz, H-6′), 6.77 (1H, d, J = 8.2 Hz, H-5′), 6.23 (1H, d, J = 15.8 Hz, H-8′), 4.74 (1H, br s, H-29a), 4.66 (1H, d, J = 12.9 Hz, H-27a), 4.62 (1H, br s, H-29b), 4.50 (1H, d, J = 12.9 Hz, H-27b), 3.66 (3H, s, OMe-28), 3.13 (1H, dd, J = 4.8, 11.4 Hz, H-3), 3.02 (1H, m, H-19), 2.45 (1H, m, H-13), 2.25 (1H, m, H-16a), 1.90 (1H, m, H-22a), 1.88 (1H, m, H-21a), 1.85 (1H, m, H-15a), 1.82 (1H, m, H-18), 1.78 (1H, m, H-12a), 1.72 (3H, s, H-30), 1.70 (1H, m, H-1a), 1.60 (2H, m, H-2), 1.55 (1H each, m, H-6a, H-7a), 1.53 (1H, m, H-11a), 1.46 (1H, m, H-22b), 1.45 (1H each, m, H-6b, H-7b), 1.42 (1H, m, H-21b), 1.37 (1H, m, H-9), 1.32 (1H each, m, H-15b, H-16b), 1.25 (1H, m, H-11b), 1.00 (3H, s, H-26), 0.99 (1H, m, H-1b), 0.97 (1H, m, H-12b), 0.92 (3H, s, H-23), 0.89 (3H, s, H-25), 0.77 (1H, m, H-5), 0.74 (3H, s, H-24); ^{13}C NMR (MeOH-d_4, 125 MHz) δ 178.1 (C, C-28), 169.4 (C, C-9′), 151.6 (C, C-20), 150.2 (C, C-4′), 147.1 (CH, C-7′), 147.0 (C, C-3′), 127.4 (C, C-1′), 123.1 (CH, C-6′), 116.5 (CH, C-5′), 115.0 (CH, C-2′), 114.9 (CH, C-8′), 110.5 (CH_2, C-29), 79.5 (CH, C-3), 64.2 (CH_2, C-27), 57.6 (C, C-17), 57.0 (CH, C-5), 53.3 (CH, C-9), 52.0 (OMe-28), 50.9 (CH, C-18), 48.4 (CH, C-19), 46.8 (C, C-14), 42.7 (C, C-8), 40.4 (CH, C-13), 40.1 (CH_2, C-1), 40.0 (C, C-4), 38.6 (C, C-10), 37.7 (CH_2, C-22), 36.6 (CH_2, C-7), 33.5 (CH_2, C-16), 31.5 (CH_2, C-21), 28.5 (CH_3, C-23), 28.0 (CH_2, C-2), 26.6 (CH_2, C-12), 25.2 (CH_2, C-15), 22.2 (CH_2, C-11), 19.6 (CH_3, C-30), 19.4 (CH_2, C-6), 17.2 (CH_3, C-25), 17.0 (CH_3, C-26), 16.1 (CH_3, C-24); HRESIMS *m*/*z* $[M + Na]^+$ 671.3903 (calcd for $C_{40}H_{56}O_7Na$, 671.3924).

Compound 2: white, amorphous solid; ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.23 (1H, d, J = 2.1 Hz, H-2′), 6.96 (1H, dd, J = 2.1, 8.2 Hz, H-6′), 6.81 (1H, d, J = 12.6 Hz, H-7′), 6.72 (1H, d, J = 8.2 Hz, H-5′), 5.72 (1H, d, J = 12.6 Hz, H-8′), 4.74 (1H, br s, H-29a), 4.67 (1H, d, J = 12.6 Hz, H-27a), 4.63 (1H, br s, H-29b), 4.36 (1H, d, J = 12.6 Hz, H-27b), 3.63 (3H, s, OMe-28), 3.13 (1H, dd, J = 5.0, 11.3 Hz, H-3), 3.02 (1H, m, H-19), 2.45 (1H, m, H-13), 2.25 (1H, m, H-16a), 1.90 (1H, m, H-22a), 1.88 (1H, m, H-21a), 1.85 (1H, m, H-15a), 1.82 (1H, m, H-18), 1.78 (1H, m, H-12a), 1.72 (3H, s, H-30), 1.70 (1H, m, H-1a), 1.60 (2H, m, H-2), 1.55 (1H each, m, H-6a, H-7a), 1.53 (1H, m, H-11a), 1.46 (1H, m, H-22b), 1.45 (1H each, m, H-6b, H-7b), 1.42 (1H, m, H-21b), 1.37 (1H, m, H-9), 1.32 (1H each, m, H-15b, H-16b), 1.25 (1H, m, H-11b), 1.00 (3H, s, H-26), 0.99 (1H, m, H-1b), 0.97 (1H, m, H-12b), 0.92 (3H, s, H-23), 0.89 (3H, s, H-25), 0.77 (1H, m, H-5), 0.74 (3H, s, H-24); and partial ^{13}C NMR (MeOH-d_4, 125 MHz) δ 169.0 (C, C-9′), 148.3 (C, C-4′), 146.0 (C, C-3′), 144.4 (CH, C-7′), 128.4 (C, C-1′), 124.3 (CH, C-6′), 118.0 (CH, C-2′), 117.2 (CH, C-8′),

115.8 (CH, C-5′), 64.1 (CH_2, C-27), 51.9 (OMe-28); HRESIMS *m/z* $[M + Na]^+$ 671.3927 (calcd for $C_{40}H_{56}O_7Na$, 671.3924).

Compound 3: white, amorphous solid; $[\alpha]^{24}_D$ −18.5 (*c* 0.006, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 6.68 (1H, d, J = 8.3 Hz, H-5″), 6.62 (1H, d, J = 2.0, H-2″), 6.60 (1H, d, J = 8.5, H-5′), 6.58 (1H, dd, J = 8.3, 2.0 Hz, H-6″), 6.47 (1H, dd, J = 1.9, 8.5, H-6′), 6.46 (1H, br s, H-2′), 3.76 (3H, s, OMe-3″), 3.70 (2H, d, J = 6.5 Hz, H-3), 3.67 (3H, s, OMe-3′), 2.97 (1H, dd, J = 5.5, 13.5 Hz, H-1a), 2.85 (1H, m, H-2), 2.67 (1H, dd, J = 9.0, 13.5 Hz, H-1b); ^{13}C NMR (MeOH-d_4, 100 MHz) δ 148.7 (C, C-3″), 148.4 (C, C-3′), 145.9 (C, C-4″), 145.4 (C, C-4′), 135.5 (C, C-1″), 133.3 (C, C-1′), 122.7 (CH, C-6′), 121.7 (CH, C-6″), 116.0 (CH, C-5″), 115.7 (CH, C-5′), 114.1 (CH, C-2′), 113.3 (CH, C-2″), 67.0 (CH_2, C-3), 56.4 (OMe-3″), 56.2 (OMe-3′), 51.7 (CH, C-2), 39.8 (CH_2, C-1); HRESIMS *m/z* $[M + Na]^+$ 327.1210 (calcd for $C_{17}H_{20}O_5Na$, 327.1208).

Compound 4: colorless needles; mp 127−128 °C (lit.[13] 128.5−129.5 °C); $[\alpha]^{25}_D$ +13.2 (*c* 0.265, $CHCl_3$) (lit.[25] $[\alpha]_D$ +9, *c* 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.24 (1H, d, J = 2.5 Hz, H-3), 6.20 (1H, d, J = 2.5 Hz, H-5), 5.14 (1H, m, H-8′), 3.25 (1H, m, H-1′a), 2.47 (1H, m, H-1′b), 1.90 (1H, m, H-7′a), 1.76 (1H, m, H-7′b), 1.60 (1H, m, H-4′a), 1.56−1.64 (2H, m, CH_2-6′), 1.50−1.62 (2H, m, CH_2-2′), 1.49 (2H, m, CH_2-3′), 1.42 (2H, m, CH_2-5′), 1.42 (1H, m, H-4′b), 1.34 (3H, d, J = 6 Hz, H-9′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.8 (C, C-7). 165.4 (C, C-2), 160.0 (C, C-4), 149.4 (C, C-6), 110.7 (CH, C-5), 105.5 (C, C-1), 101.3 (CH, C-3), 75.1 (CH, C-8′), 33.5 (CH_2, C-1′), 31.0 (CH_2, C-7′), 30.7 (CH_2, C-2′), 27.2 (CH_2, C-3′), 24.6 (CH_2, C-6′), 24.1 (CH_2, C-5′), 21.1 (CH_2, C-4′), 20.1 (CH_3, C-9′); HREIMS *m/z* $[M]^+$ 278.1519 (calcd for $C_{16}H_{22}O_4$, 278.1518).

Compound 5: yellowish, amorphous solid; $[\alpha]^{22}_D$ +17.2 (*c* 0.14, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.55 (1H, d, J = 15.8 Hz, H-7′), 7.04 (1H, d, J = 1.7 Hz, H-2′), 6.94 (1H, dd, J = 1,7 8.2 Hz, H-6′), 6.77 (1H, d, J = 8.2 Hz, H-5′), 6.31 (1H, d, J = 15.8 Hz, H-8′), 5.25 (1H, t, J = 3.4 Hz, H-12), 4.60 (1H, d, J = 9.5 Hz, H-3), 3.83 (1H, ddd, J = 4.4, 9.5, 11.7 Hz, H-2), 2.86 (1H, dd, J = 3.0, 13.5 Hz, H-18), 2.00 (1H, dd, J = 4.4, 11.7 Hz, H-1a), 1.99 (1H, m, H-16a), 1.96 (2H, m, H-11), 1.80 (1H, m, H-15a), 1.74 (1H, m, H-22a), 1.70 (1H, m, H-9), 1.68 (1H, m, H-19a), 1.60 (1H, m, H-16b), 1.57 (1H, m, H-6a), 1.54 (2H, m, H-7a/H-22b), 1.46 (1H, m, H-6b), 1.38 (1H, m, H-21a), 1.35 (1H, m, H-7b), 1.19 (1H, m, H-21b), 1.18 (3H, s, H-27), 1.13 (1H, m, H-19b), 1.07 (1H, m, H-15b), 1.05 (3H, s, H-25), 1.04 (1H, m, H-1b), 0.99 (1H, m, H-5), 0.94 (6H, s, H-24/H-30), 0.90 (3H, s, H-29), 0.89 (3H, s, H-23), 0.84 (3H, s, H-26); ^{13}C NMR (MeOH-d_4, 125 MHz) δ 182.5 (C, C-28), 169.5 (C, C-9′), 149.4 (C, C-4′), 146.7 (C, C-3′), 146.5 (CH, C-7′), 145.5 (C, C-13), 127.8 (C, C-1′), 123.0 (CH, C-12), 122.7 (CH, C-6′), 116.4 (CH, C-5′), 115.7 (CH, C-8′), 115.0 (CH, C-2′), 85.4 (CH, C-3), 67.5 (CH, C-2), 56.4 (CH, C-5), 48.9 (CH, C-9), 48.5 (CH_2, C-1), 47.8 (C, C-17), 47.3 (CH_2, C-19), 42.9 (CH, C-18), 42.8 (C, C-14), 40.6 (C, C-4), 40.5 (C, C-8), 39.2 (C, C-10), 34.9 (CH_2, C-21), 33.8 (CH_2, C-22), 33.7 (CH_2, C-7), 33.5 (CH_3, C-29), 31.6 (C, C-20), 29.1 (CH_3, C-23), 28.8 (CH_2, C-15), 26.3 (CH_3, C-27), 24.5 (CH_2, C-11), 24.0 (CH_2, C-16), 23.9 (CH_3, C-30), 19.4 (CH_2, C-6), 18.2 (CH_3, C-24), 17.7 (CH_3, C-26), 17.0 (CH_3, C-25); HRESIMS *m/z* $[M + Na]^+$ 657.3756 (calcd for $C_{39}H_{54}O_7Na$, 657.3767).

Compound 6: white, amorphous powder; $[\alpha]^{22}_D$ +3.42 (*c* 0.19, MeOH); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.55 (1H, d, J = 15.8 Hz, H-7′), 7.04 (1H, d, J = 2.0 Hz, H-2′), 6.94 (1H, dd, J = 2,0 8.2 Hz, H-6′), 6.77 (1H, d, J = 8.2 Hz, H-5′), 6.31 (1H, d, J = 15.8 Hz, H-8′), 5.24 (1H, t, J = 3.4 Hz, H-12), 4.62 (1H, d, J = 10.0 Hz, H-3), 3.83 (1H, ddd, J = 4.4, 10.0, 12.1 Hz, H-2), 2.22 (1H, d, J = 11.3 Hz, H-18), 2.03 (1H, dd, J = 4.4, 12.1 Hz, H-1a), 2.00 (1H, m, H-16a), 1.97 (2H, m, H-11a/H-11b), 1.95 (1H, m, H-15a), 1.70 (1H, m, H-22a), 1.66 (1H, m, H-9), 1.65 (1H, m, H-16b), 1.63 (1H, m, H-22b), 1.59 (1H, m, H-7a), 1.57 (1H, m, H-6a), 1.50 (1H, m, H-21a), 1.46 (1H, m, H-6b), 1.38 (1H, m, H-7b), 1.37 (1H, m, H-19), 1.34 (1H, m, H-21b), 1.14 (3H, s, H-27), 1.08 (1H, m, H-15b), 1.07 (3H, s, H-25), 1.04 (1H, m, H-1b), 1.00 (1H, m, H-20), 0.99 (1H, m, H-5), 0.95 (3H, d, J = 5.4 Hz, H-29), 0.94 (3H, s, H-24), 0.89 (3H, s, H-23), 0.88 (3H, d, J = 6.2 Hz, H-30), 0.87 (3H, s, H-26); ^{13}C NMR (MeOH-d_4, 188 MHz) δ 182.4 (C, C-28), 169.6 (C, C-9′), 149.5 (C, C-4′), 146.8 (C, C-3′), 146.6 (CH, C-7′), 140.0 (C, C-13), 127.9 (C, C-1′), 126.4 (CH, C-12), 122.9 (CH, C-6′), 116.5 (CH, C-5′), 115.8 (CH, C-8′), 115.1 (CH, C-2′), 85.6 (CH, C-3), 67.6 (CH, C-2), 56.5 (CH, C-5), 54.5 (CH, C-18), 49.5 (C, C-17), 48.9 (CH, C-9), 48.7 (CH_2, C-1), 43.4 (C, C-14), 40.8 (C, C-8), 40.6 (C, C-4), 40.5 (CH, C-19), 40.4 (CH, C-20), 39.2 (C, C-10), 38.2 (CH_2, C-22), 34.2 (CH_2, C-7), 31.9 (CH_2, C-21), 29.3 (CH_3, C-23/C-15), 25.4 (CH_2, C-16), 24.5 (CH_2, C-11), 24.1 (CH_3, C-27), 21.6 (CH_3, C-29), 19.4 (CH2, C-6), 18.4 (CH_3, C-24), 17.9 (CH_3, C-26), 17.2 (CH_3, C-25); HRESIMS *m/z* $[M + Na]^+$ 657.3785 (calcd for $C_{39}H_{54}O_7Na$, 657.3767).

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Supporting Information Available: Figures S1−S8. ^{1}H and ^{13}C NMR data for compounds **1**, **2**, **3**, **5**, and **6**, and spectroscopic data and characterization details for known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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