Chemical Constituents from *Drypetes littoralis*

Mei-Tsu Lin, Lih-Chun Chen, Chien-Kuang Chen, Karin C. S. Chen Liu, and Shoei-Sheng Lee*

School of Pharmacy, College of Medicine, National Taiwan University, Taipei 100, Taiwan, Republic of China

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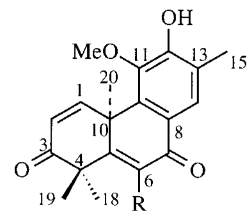
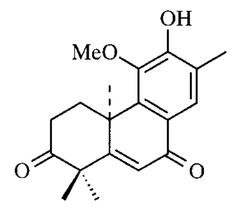
Chemical investigation of *Drypetes littoralis* yielded three new tricyclic diterpenes, drypetenones A, B, and C (**1**−**3**), and one new xanthone (**4**). Spectral analyses and chemical correlations established the structures as 10*S*-12-hydroxy-11-methoxy-13-methylpodocarpa-1,5,8,11,13-pentaene-3,7-dione, (**1**), 10*S*-12-hydroxy-11-methoxy-13-methylpodocarpa-5,8,11,13-tetraene-3,7-dione (**2**), 10*S*-12-hydroxy-6,11-dimethoxy-13-methylpodocarpa-1,5,8,11,13-pentaene-3,7-dione (**3**), and 1-hydroxy-7-hydroxymethyl-6-methoxyxanthone (**4**). Complete ^{13}C NMR assignment of boehmenan D (**5**) is also made.

Drypetes littoralis (C. B. Rob.) Merr. (Euphorbiaceae), an evergreen tree, is one of three species of *Drypetes* found in Taiwan.[1] The chemical constituents of *D. hieranensis*, one of these three species, have been studied, and some of them have been reported.[2] The MeOH extract of this species was found to possess activity against Epstein Barr virus DNA polymerase in a preliminary study.[3] This background prompted us to explore the phytochemistry of *D. littoralis*, and the results are reported here.



1 R= H
3 R= OMe



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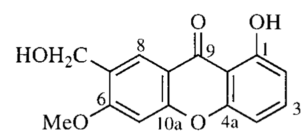

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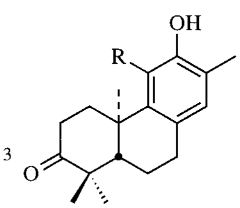
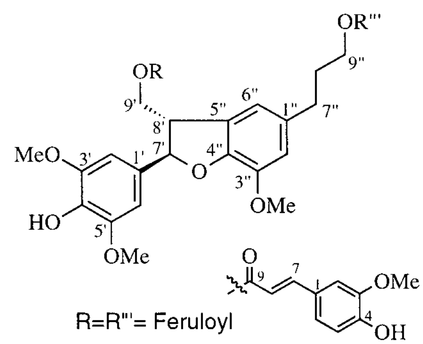


6 R= OMe
7 R= H



R=R'''= Feruloyl

5

Results and Discussion

An ethanolic extract of the stem of *D. littoralis* was triturated with H_2O to give water-soluble and -insoluble fractions. The insoluble fraction was then triturated with 50% aqueous EtOH to yield a soluble fraction, which upon column chromatography resulted in isolation of compounds **1**−**4**.

Compounds **1**−**3** had UV absorption maxima at 250 and 315 nm, the latter showing significant bathochromic shift under strong alkaline conditions, indicating the presence of phenolic functions. Their IR spectra displayed absorption for hydroxyl (3300 cm^{-1}), aromatic (1500−1600 cm^{-1}), and α,β-unsaturated carbonyl (1690 cm^{-1}) groups. These were similar to those of podocarpa-5,8,11,13-tetraene-3,7-diones, such as teuvincenone A.[4]

Compound **1** had the molecular formula $C_{19}H_{20}O_4$, as deduced from its HREIMS. The olefinic and aromatic regions of its ^{1}H NMR spectrum revealed four signals, two appearing as an AX system at δ 6.12 and 7.73, $J_{AX} = 10.2$ Hz, assignable to Hα and Hβ of an α,β-conjugated carbonyl system. The remaining ^{1}H NMR signals included one MeO− singlet (δ 3.97) and four methyl singlets (δ 2.31, 1.70, 1.55, and 1.38). The arrangement of these substituents was determined by analysis of its NOESY spectrum, which showed the following key NOEs: δ 6.12 (H-2) ↔ δ 7.73 (H-1) ↔ δ 1.70 (H-20); δ 7.73 (H-1) ↔ δ 3.97 (11-OMe) ↔ δ 1.70 (H-20); δ 1.55 (H-19) ↔ δ 6.47 (s, H-6) ↔ δ 1.38 (H-18) ↔ δ 1.55 (H-19); δ 7.82 (s, H-14) ↔ δ 2.31 (H-15). These data established compound **1** as 12-hydroxy-11-methoxy-13-methylpodocarpa-1,5,8,11,13-pentaene-3,7-dione.

Compound **2** had the molecular formula $C_{19}H_{22}O_4$, as deduced from its HREIMS, two hydrogen atoms more than **1**. Comparison of the ^{13}C NMR data with those of **1** revealed that the carbon signals of the α,β-conjugated carbonyl system in **1** were replaced by two methylenes (δ_C 28.5, 33.1) and a nonconjugated carbonyl (δ 213.3) in **2**. Except for these differences, the rest of the signals were closely similar, indicating that **2** was a 1,2-dihydrogenated analogue of **1**. This was confirmed by the NOE between H-20 (δ 1.42, s) and H-1β (δ 3.08, ddd, $J = 13.7$, 6.6, 4.4 Hz). An HMBC spectrum of **2** displaying a three-bond coupling between H-20 (δ 1.42) and C-1 (t, δ 28.5) was also supportive. Hence, **2** was established to be 12-hydroxy-11-methoxy-13-methylpodocarpa-5,8,11,13-tetraene-3,7-dione.

Compound **3** had the molecular formula $C_{20}H_{22}O_5$, as deduced from the HREIMS, an OCH_2 unit more than that of compound **1**. Comparison of its ^{1}H NMR spectrum with

* To whom correspondence should be addressed. Tel: 886-2-23916127. Fax: 886-2-23919098. E-mail: shoeilee@ha.mc.ntu.edu.tw.

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that of **1** revealed that the H-6 singlet at δ 6.47 in **1** was replaced by a MeO singlet (δ 3.87) in **3**. The ^{13}C NMR spectrum also reflected this difference by an additional oxygenated signal (s, δ 148.2) and an MeO signal (q, δ 61.0) instead of an olefinic methine (d, δ 124.3), suggesting that **3** was 12-hydroxy-6,11-dimethoxy-13-methylpodocarpa-1,5,8,11,13-pentaene-3,7-dione. This proposed structure was confirmed by an NOE between H-18 (δ 1.50), H-19 (δ 1.65), and 6-OMe (δ 3.87).

The stereochemistry at C-10 of compounds **1**−**3** was determined by comparison of the specific optical rotation of the catalytic hydrogenation product (**6**) of **2** with data reported for very similar known compounds. NOED studies on **6** suggested a trans junction for rings A and B since there was no enhancement of H-5 upon irradiation at the 10-Me (i.e., H-20) frequency. The trans A/B ring junction and the negative rotation, $[\alpha]^{25}_{D}$ −127.0° (*c* 1.0, MeOH), similar to those for (−)-5*R*,10*S*-12-hydroxy-13-methylpodocarpa-8,11,13-trien-3-one (**7**),[5,6] established a 5*R*,10*S*-stereochemistry for **6**. Consequently, **2** possesses the 10*S*-configuration. Compounds **1** and **3**, having the same sign of optical rotation and the same plant origin as **2**, are assumed to possess the same stereochemistry at C-10.

Compound **4** had the molecular formula $C_{15}H_{12}O_5$, as deduced from the HREIMS, suggesting 10 double bond and ring equivalents. It contained a 1-hydroxyxanthone moiety, as evidenced by characteristic UV spectral data[7,8] and by a D_2O-exchangeable ^{1}H NMR signal at δ 12.69 (δ_{1-OH}). It is 1,6,7-trisubstituted, as exemplified by the ^{1}H NMR spectrum (DMSO-d_6), which showed signals for three adjacent aryl protons, appearing as an AMX system (δ_A 6.81, dd, H-2; δ_M 7.09, H-4, dd; δ_X 7.71, dd, H-3; J_{AM} = 0.8 Hz, J_{AX} = 8.2 Hz, J_{MX} = 8.4 Hz), and two aryl protons *para* to each other (δ 7.49, s; δ 7.62, t, J = 1.3 Hz). The other signals included an MeO singlet (δ 3.91) and an oxygenated methylene doublet (δ 4.63, J = 1.3 Hz) which coupled benzylically to the aryl proton at δ 7.62. This aryl proton was observed to couple to the C-9 carbonyl (δ 181.3) in an HMBC spectrum. NOED experiments showed NOE between H-8 (δ 7.62) and 7-CH_2OH (δ 4.63), and H-5 (δ 7.49) and MeO-6 (δ 3.91). Consequently, **4** was concluded to be 1-hydroxy-7-hydroxymethyl-6-methoxyxanthone.

Complete ^{1}H and ^{13}C NMR data of **1**−**4** were assigned from NOED and 2D NMR techniques and are listed in the Experimental Section. To our knowledge, compounds **1**−**4** are new natural products. Compounds **1**−**3** were named drypetenones A, B, and C, respectively.

Nine known compounds were also isolated. They were amentoflavone,[9,10] coniferaldehyde,[11] sinapaldehyde,[12] lariciresinol,[13,14] syringaresinol,[15] the neolignans boehmenan[16] and boehmenan D (**5**), friedelin,[17] and β-amyrin,[17] the latter two being from the 50% aqueous EtOH-insoluble fraction. They were identified by comparison of the spectral data with those reported. Boehmenan D (**5**) has been isolated recently from *Ochroma lagopus* (Bombacaceae).[16] Although the ^{1}H NMR spectrum of **5** was reported, the ^{13}C NMR spectrum was not. The ^{13}C NMR data for **5** are included in the present report as Supporting Information.

Experimental Section

General Experimental Procedures. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1760-X infrared Fourier transform spectrophotometer (KBr). UV spectra were measured in MeOH on a Hitachi 150-20 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 FT spectrometer in $CDCl_3$ (δ_H 7.24, δ_C 77.0) or DMSO-d_6 (δ_H 2.49, δ_C 39.5), using Bruker's standard pulse programs: in the HMQC and HMBC experiments, Δ = 1 s and J = 140, 10 Hz, respectively, the correlation maps consisted of 512 × 1K data points per spectrum, each composed of 16−64 transients. MS were recorded on a JEOL JMX-HX 110 spectrometer. Centrifugal partition chromatography (CPC) was performed with a CPC-LLN instrument, Model-NMF, Sanki Engineering Limited, Kyoto, Japan, using the upper and lower layers of solvent system A, $CHCl_3$−MeOH−H_2O−^{i}PrOH (10:10:6:1), as mobile and stationary phases, respectively. Silica gel for column chromatography was finer than 230 mesh unless otherwise specified.

Plant Material. The stems of *D. littoralis* for this study were collected from Kan-Din National Park, Taiwan, in September 1995. A voucher specimen (No. NTUPH19950901) has been deposited in the School of Pharmacy, National Taiwan University.

Extraction and Isolation. The ground, dry stems (22.7 kg) were extracted with 95% EtOH (60 L × 4). The ethanolic residue (386 g) was triturated successively with water (1 L × 2) and 50% aqueous EtOH to give an H_2O-soluble fraction (A), a 50% EtOH-soluble fraction (B, 20 g), and a residue (C, 92.7 g). The 50% EtOH-soluble fraction was chromatographed over Sephadex LH-20, eluted with MeOH, to give six fractions (I−VI). Of these, fraction V (7.9 mg) was found to be amentoflavone.[9,10] Fraction II (7.34 g) was subsequently fractionated with CPC delivered by the solvent system A as indicated above to give five subfractions. Chromatography of subfraction 2 (931 mg) on silica gel (40 g), eluted with MeOH (0−20%) in $CHCl_3$, gave coniferaldehyde[11] (15 mg) and sinapaldehyde[12] (5 mg) and a fraction (24.9 mg) containing lariaresinol[13,14] (4.4 mg), which was purified via a Sephadex LH-20 column [8 g, MeOH−$CHCl_3$ (1:1)] and a preparative TLC plate [1 mm, Me_2CO−toluene (3:7)]. Chromatography of subfraction 4 (1.60 g) on silica gel (80 g), eluted with acetone (0−20%) in hexane, gave five subfractions. Subfraction 2 was further separated by a silica gel column (20 g), eluted with EtOAc−hexane (1:9), to give compounds **3** (9 mg), **1** (106 mg), and **2** (108 mg). Subfraction 3 (70 mg) was further separated by a silica gel column (230−400 mesh, 6 g), eluted with EtOAc−hexane (1:3), to give syringaresinol[15] (21 mg). Fraction III (872 mg) was subjected to two successive columns (silica gel for PTLC, 40 and 8 g), eluted with Me_2CO−toluene (1:9) and EtOAc−toluene (2:8), respectively, to afford compound **4** (2.3 mg), boehmenan[16] (70 mg), and boehmenan D[16] (**5**, 12 mg). The known compounds were identified by comparison with reference compounds and literature values.

12-Hydroxy-11-methoxy-13-methylpodocarpa-1,5,8,11,-13-pentaene-3,7-dione (1): R_f 0.63 [(EtOAc−hexane (1:1)], mp 216−220 °C; $[\alpha]^{25}_{D}$ −130° (*c* 0.5, MeOH); UV λ_{max} (log ϵ) 271 (3.97), 319 (3.96) nm; (MeOH + NaOH) 255 (4.22), 397 (4.12) nm; IR ν_{max} 3307, 2978, 2940, 1689, 1639, 1603, 1556, 1483, 1463, 1429, 1381, 1360, 1333, 1304, 1265, 1202, 1165, 1130, 1093, 1052, 922, 897, 806, 792, 765, 713, 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82 (1H, s, H-14), 7.73 (1H, d, J = 10.2 Hz, H-1), 6.47 (1H, s, H-6), 6.12 (1H, d, J = 10.2 Hz, H-2), 3.97 (3H, s, 11-OMe), 2.31 (3H, s, H-15), 1.70 (3H, s, H-20), 1.55 (3H, s, H-19), 1.38 (3H, s, H-18); ^{13}C NMR ($CDCl_3$) δ 201.1 (s, C-3), 184.0 (s, C-7), 167.6 (s, C-5), 151.5 (d, C-1), 152.9 (s, C-12), 144.6 (s, C-11), 137.8 (s, C-9), 126.8 (d, C-2), 126.4 (s, C-13), 124.9 (d, C-14), 124.3 (d, C-6), 123.1 (s, C-8), 60.8 (q, 11-OMe), 49.0 (s, C-4), 42.7 (s, C-10), 33.5 (q, C-20), 28.8 (q, C-18), 28.0 (q, C-19), 15.7 (q, C-15); HMBC data ($CDCl_3$) C-1 to H-20, C-3 to H-1, H-18 and -19, C-4 to H-2, -6, -18, and -19, C-5 to H-18, -19, -20, and -1, C-7 to H-14, C-8 to H-6, C-9 to H-1, -14, and -20, C-10 to H-1, -2, -6, and -20, C-11 to 11-O*Me*, C-12 to H-14 and -15, C-13 to H-15, C-14 to H-15, C-15 to H-14, C-18 to H-19, C-19 to H-18, C-20 to H-1; EIMS (20 eV) *m/z* (rel int) [M]$^+$ 312 (100), 297 (43), 269 (37), 254 (5), 218 (12), 203 (3); HREIMS *m/z* [M]$^+$ 312.1353 (calcd for $C_{19}H_{20}O_4$, 312.1362).

12-Hydroxy-11-methoxy-13-methylpodocarpa-5,8,11,-13-tetraene-3,7-dione (2): R_f 0.48 [(EtOAc−hexane (1:1)], mp 165−168 °C; $[\alpha]^{25}_{D}$ −173° (*c* 0.5, MeOH); IR ν_{max} 3284, 2982, 2939, 1692, 1646, 1600, 1556, 1463, 1427, 1386, 1362, 1328, 1287, 1260, 1202, 1157, 1125, 1101, 1058, 931, 910, 891, 817, 775, 713, 679 cm^{-1}; UV λ_{max} (log ϵ) 315 (3.98); λ_{max} (MeOH+NaOH) 244 (4.34), 398 (4.11) nm; ^{1}H NMR ($CDCl_3$) δ 7.85 (1H, s, H-14), 6.42 (1H, s, H-6), 3.88 (3H, s, 11-OMe), 3.07 (1H, ddd, J = 13.7, 6.6, 4.4 Hz, H-1β), 2.70 (1H, m) and 2.72 (1H, m) (H-2's), 2.30 (3H, s, H-15), 1.94 (1H, ddd, J = 13.7, 9.6, 9.6 Hz, H-1α), 1.44 (3H, s, H-19), 1.42 (3H, s, H-20), 1.38 (3H, s, H-18); ^{13}C NMR ($CDCl_3$) δ 213.3 (s, C-3), 184.3 (s, C-7), 173.0 (s, C-5), 152.7 (s, C-12), 145.1 (s, C-11), 140.1 (s, C-9), 125.8 (s, C-13), 124.8 (d, C-14), 123.3 (d, C-6), 122.9 (s, C-8), 60.7 (q, 11-OMe), 49.6 (s, C-4), 40.6 (s, C-10), 33.1 (t, C-2), 29.7 (q, C-18), 28.5 (t, C-1), 26.5 (q, C-19), 22.4 (q, C-20), 15.5 (q, C-15); HMBC data ($CDCl_3$) H-1's to C-2, C-3, C-5, C-9, C-10 and C-20, H-2's to C-1, C-3 and C-10, H-6 to C-4, C-5 and C-10, H-14 to C-7, C-9, C-12 and C-15, H-15 to C-12, C-13, and C-14, H-18 to C-3, C-4, C-5 and C-19, H-19 to C-3, C-4, C-5 and C-18, H-20 to C-1, C-5, C-9 and C-10, 11-OCH_3 to C-11; NOESY data ($CDCl_3$) 11-OMe ↔ H-20 ↔ H-1β (3.08) ↔ H-2's; H-2β ↔ H-19; H-1α (1.91) ↔ H-1β ↔ 11-OMe, H-14 ↔ H-15, H-19 ↔ H-6 ↔ H-18; NOED data ($CDCl_3$) H-18 to H-1α (7.1%), H-2α (4.6%), H-6 (16.4%), H-19 (6.9%), H-19 to H-2β (2.7%), H-6 (12.2%), H-18 (δ 1.38) (4.2%), H-20 (1.7%), H-20 (δ 1.42) to H-1β (δ 3.07) (4.8%), H-2β (5.1%), 11-OMe (8.2%), H-19 (δ 1.44) (3.0%); EIMS (20 eV) m/z (rel int) $[M]^+$ 314 (100), 299 (20), 271 (15), 258 (30), 243 (5), 231 (3); HREIMS m/z $[M]^+$ 314.1516 (calcd for $C_{19}H_{22}O_4$, 314.1519).

12-Hydroxy-6,11-dimethoxy-13-methylpodocarpa-1,5,8,-11,13-pentaene-3,7-dione (3): R_f 0.43 [(EtOAc−hexane (2:3)], mp 182−185 °C (EtOAc−hexane); $[\alpha]^{25}_D$ −115° (c 0.5, MeOH); UV λ_{max} (log ϵ) 245 (4.2), 313 (3.98); (MeOH+NaOH) 211 (4.93), 248 (4.23), 393 (4.13) nm; IR ν_{max} 3240, 2977, 2939, 1715, 1650, 1590, 1556, 1469, 1384, 1349, 1243, 1204, 1154, 1050, 933, 896, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (1H, s, H-14), 7.54 (1H, d, J = 10.2 Hz, H-1), 6.19 (1H, d, J = 10.2 Hz, H-2), 3.95 (3H, s, 11-OMe), 3.87 (3H, s, 6-OMe), 2.31 (3H, s, H-15), 1.66 (3H, s, H-19), 1.61 (3H, s, H-20), 1.50 (3H, s, H-18); ^{13}C NMR ($CDCl_3$) δ 202.6 (s, C-3), 180.0 (s, C-7), 148.4 (s, C-5), 150.6 (d, C-1), 152.2 (s, C-12), 148.2 (s, C-6), 144.0 (s, C-11), 137.1 (s, C-9), 127.3 (d, C-2), 126.1 (s, C-13), 125.1 (d, C-14), 123.9 (s, C-8), 61.0 (q, 11-OMe), 59.6 (q, 6-OMe), 49.2 (s, C-4), 42.2 (s, C-10), 34.1 (q, C-20), 28.0 (q, C-18), 22.2 (q, C-19), 15.5 (q, C-15); HMBC data H-1 to C-3, C-5, C-9, and C-10, H-2 to C-4 and C-10, H-14 to C-7, C-9, and C-15, H-15 to C-12, C-13, and C-14, H-18 to C-3, C-4, C-5 and C-19, H-19 to C-3, C-4, C-5 and C-18, H-20 to C-1, C-5, C-9 and C-10, 6-OMe to C-6, 11-OCH_3 to C-11; NOED data 11-OMe to H-1 (3.1%) and H-20 (4.7%), 6-OMe to H-19 (1.9%), H-20 to 11-OMe (3.6%), H-18 to H-19 (4.8%) and 6-OMe (1.8%), H-15 to H-14 (10.0%), H-19 to H-18 (5.1%) and 6-OMe (3.0%); EIMS (20 eV) m/z (rel int) $[M]^+$ 342 (100), 311 (37), 299 (16), 283 (21), 241 (43), 218 (5); HREIMS m/z $[M]^+$ 342.1463 (calcd for $C_{20}H_{22}O_5$, 342.1468).

1-Hydroxy-7-hydroxymethyl-6-methoxyxanthone (4): R_f 0.62 [(EtOAc−toluene (1:1)], mp 180−183 °C (amorphous); UV λ_{max} (log ϵ) 235 (4.00), 260 (4.09), 378 (3.48); (MeOH+NaOH) λ_{max} (log ϵ) 235 (4.04), 262 (4.02), 380 (3.42) nm; IR ν_{max} 2490, 1644, 1479, 1433, 1391, 1237, 1207, 1168, 1055, 809, 759, 717 cm^{-1}; ^{1}H NMR (DMSO-d_6) see text; ^{13}C NMR (DMSO-d_6) δ 181.3 (s, C-9), 160.8 (s, C-1), 155.7 (s, C-4a), 152.8 (s, C-6), 150.8 (s, C-10a), 142.4 (s, C-7), 137.1 (d, C-3), 118.4 (s, C-8a), 115.5 (d, C-8), 109.8 (d, C-2), 108.0 (s, C-9a), 107.3 (d, C-4), 102.9 (d, C-5), 58.0 (t, C-7a), 55.9 (q, 6-OMe); HMBC (DMSO-d_6) C-1 to H-2, -3 and 1-OH, C-2 to H-4, 1-OH, C-4 to H-2, C-4a to H-3, C-6 to H-5, 6-OMe, H-8, C-7 to H-5, -8, 7-CH_2, C-8 to 7-CH_2, C-8a to H-5, -8, C-9 to H-8, C-9a to H-4, C-10a to H-5, -8, C-7a to H-8, -5; NOED data 6-OMe to H-5 (4.5%), 7-CH_2OH to 8-H (1.5%); EIMS (20 eV) m/z (rel int) $[M]^+$ 272 (100), 243 (23), 229 (23), 211 (6), 201 (8), 155 (13), 127 (10); HREIMS m/z $[M]^+$ 272.0674 (calcd for $C_{15}H_{12}O_5$, 272.0685).

Preparation of 12-Hydroxy-11-methoxy-13-methylpodocarpa-8,11,13-trien-3-one (6). A mixture of **3** (10.3 mg), EtOAc (2 mL), and Pd−C (10%, 5 mg) was catalytically hydrogenated under 1 atm of hydrogen at room temperature for 1 day.[18] Usual workup and further separation on a silica gel column, eluted with 2% Me_2CO in toluene, yielded compound **6** (8.9 mg): $[\alpha]^{25}_D$ −127.0° (c 1.0, MeOH); ^{1}H NMR ($CDCl_3$) δ 6.62 (1H, s, H-14), 5.02 (s, 12-OH), 3.79 (3H, s, 11-OMe), 2.93 (1H, ddd, J = 6.1, 8.0, 13.9 Hz, H-1β), 2.77 (2H, m, H-7), 2.66 (1H, ddd, J = 6.0, 9.5, 15.1 Hz, H-2α), 2.49 (1H, ddd, J = 6.1, 8.5, 15.1 Hz, H-2β), 2.18 (3H, s, H-15), 1.98 (1H, m, H-1α), 1.97 (1H, dd, J = 2.1, 12.3 Hz, H-5), 1.73 (1H, ddt, J = 12.2, 5.6, 2.1 Hz, H-6α), 1.59 (1H, dq, J = 6.0, 12.2 Hz, H-6β), 1.25 (3H, s, H-20), 1.14 (3H, s, H-18), 1.12 (3H, s, H-19); NOED data ($CDCl_3$) H-20 to H-1β (4.4%), -2β (2.3%), -19 (5.7%), -6β (5.7%), and 11-OCH_3 (3.3%), H-18 to H-2α (3.9%), -5 (10.3%), -6α (5.0%), -6β (−1.3%), and -19 (2.9%), H-19 to H-2β (1.1%), -18 (2.5%), -6β (3.7%), and -20 (5.8%); ^{13}C NMR ($CDCl_3$) δ 218.5 (s, C-3), 146.4 (s, C-11), 145.9 (s, C-12), 137.1 (s, C-9), 127.7 (s, C-8), 126.6 (d, C-14), 123.7 (s, C-13), 60.7 (q, 11-MeO), 52.1 (d, C-5), 47.3 (s, C-4), 38.3 (s, C-10), 36.6 (t, C-1), 34.3 (t, C-2), 31.5 (t, C-7), 28.2 (q, C-18), 22.2 (q, C-20), 20.6 (t, C-6), 20.5 (q, C-19), 15.2 (q, C-15); HMBC data ($CDCl_3$) C-1 to H-20, and −2's, C-2 to H-1β, C-3 to H-18 and -19, C-4 to H-2β, -18, -19, and -5, C-5 to H-18, -19, -20, and -1β, C-6 to H-7's, C-7 to H-5, -6β, and -14, C-8 to H-7's, C-9 to H-7's, -20, and -14, C-10 to H-1's, -2's, -5, and -20, C-11 to 11-OMe and 12-OH, C-12 to 12-OH, H-14 and -15, C-13 to H-15, C-14 to H-15, C-15 to H-14, C-18 to H-19 and -5, C-19 to H-18, C-20 to H-1's.

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Supporting Information Available: ^{1}H and ^{13}C NMR data and HMBC data of boehmenan D (**5**) measured in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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