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ARTICLE *in* JOURNAL OF NATURAL PRODUCTS · JULY 2009

Impact Factor: 3.8 · DOI: 10.1021/np800594a · Source: PubMed

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Triterpenoids and a Lignan from the Aerial Parts of *Maytenus apurimacensis*

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Received September 22, 2008

Five new triterpenes (**1**−**5**) and one new lignan (**6**) were isolated from the aerial parts of *Maytenus apurimacensis*. Their structures were determined on the basis of spectroscopic studies, including homonuclear and heteronuclear correlation NMR experiments (COSY, ROESY, HSQC, and HMBC).

Throughout the ages, plants have been the basis of traditional medicines.[1] As part of a search for new bioactive compounds from species used in South American folk medicine, we have extensively investigated species belonging to the Celastraceae family, isolating novel compounds with a wide variety of structures and biological activities. For example, *Maytenus macrocarpa* provided the so-called macrocarpines, with significant antitumoral activity,[2] and *M. amazonica* yielded new bioactive triterpenes related to 22β-hydroxytingenone.[3] Recently, we have also reported the isolation and chemical characterization of new sesquiterpenes from the root bark of *M. apurimacensis*.[4] These agarofuran sesquiterpenes exhibited high anti-MDR activity.[4] In the present work we give an account of the phytochemical analysis of the ethanolic extract of the aerial parts of *M. apurimacensis,* which yielded four new lupane-type terpenoids (**1**−**4**), a new glutinane triterpene (**5**), and a new lignan (**6**). *M. apurimacensis* also yielded the triterpenes calenduladiol,[5] 3-epicalenduladiol,[6] and resinone,[7] the diterpene vierol,[8] the monoterpene loliolide,[9] and the lignan *trans*-divanillyltetrahydrofuran.[10] Their structures were elucidated by means of ^{1}H and ^{13}C NMR spectroscopic studies, including homonuclear (COSY and ROESY) and heteronuclear correlation (HSQC and HMBC) experiments.

Results and Discussion

Repeated chromatography on silica gel and Sephadex LH-20 of an EtOH extract from the leaves of *M. apurimacensis* yielded six new compounds (**1**−**6**), together with the known compounds mentioned above.

Compound **1** was isolated as an amorphous, white solid, with the molecular formula $C_{30}H_{50}O_3$ assigned by HRMS. The IR spectrum revealed the presence of hydroxy groups (3369 cm^{-1}). Its ^{1}H NMR spectrum (Table 1) showed five methyl groups [δ 1.05, 1.00, 0.95, 0.84 and 0.82], an isopropenyl group [δ 1.68 (3H, s), 4.69 (1H, s), and 4.60 (1H, s)], two oxymethine protons [δ 3.82 (1H, dd, J = 11.5, 4.2 Hz), 3.38 (1H, m)], a CH_2OH group [δ 4.16 (1H, d, J = 11.2 Hz), 3.38 (1H, m)], and the typical lupane H$_\beta$-19 proton signal at δ 2.42 (1H, m). All these data indicate that compound **1** is a lupane triterpene with three hydroxy groups. Its ^{13}C NMR and DEPT spectra (Table 2) showed the presence of a CH_2 and two CH groups bearing a hydroxy functionality (δ 61.2, 76.2, and 79.7, respectively). The $\Delta^{20,29}$ functionality of a lupane skeleton was also confirmed by the presence of the two sp^2 carbons at δ 149.6 (s) and 110.0 (t). The positions of the secondary hydroxy groups at δ 3.38, 3.82, and 4.16 were established by the ^{1}H−^{13}C long-range correlations detected in the HMBC spectrum. Thus, the positions of the C-3, C-16, and C-28 hydroxy groups were determined from the following HMBC correlations: H-23/C-3, H-23/C-4, H-24/C-3, H-24/C-4, H-16/C-28, H-16/C-14, H-28/C-16, H-28/C-17, and H-28/C-22.

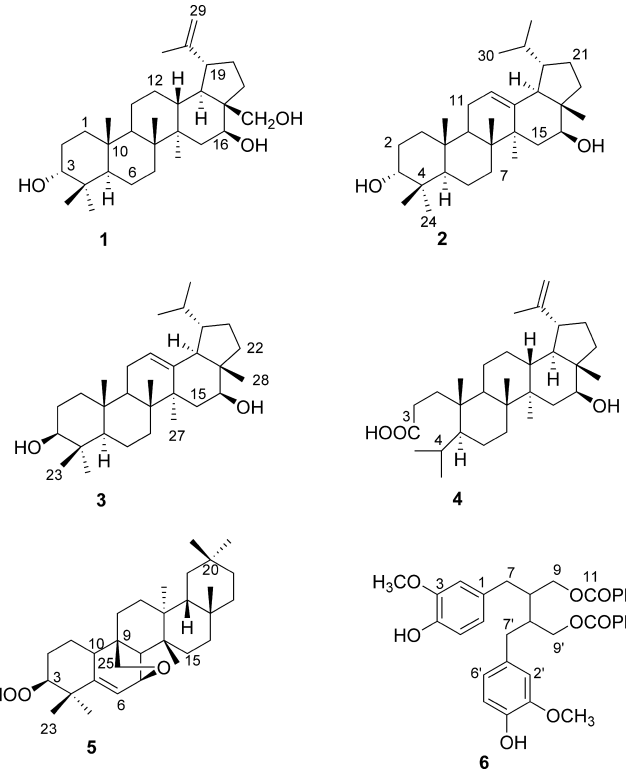

Figure 1. Structure of the new compounds (**1**−**6**).

The orientation of the C-3 oxymethine proton was established as β by the NOE effects between H-3 and Me-23 and Me-24, which indicated an equatorial position for H-3 on the β-face and an axial orientation for the hydroxy group on the α-face. Similarly, the orientation of the C-16 hydroxy group was assigned as α by the NOE effect between H-16 and Me-27. All of these data and comparison with the data of 3-epicalendualdiol[6] established the structure of **1** as 28-hydroxy-3-epicalenduladiol.

Compounds **2** and **3** showed the same molecular formula, $C_{30}H_{50}O_2$, and similar spectroscopic data (Tables 1 and 2). Their IR spectra showed the presence of hydroxy groups. The ^{1}H NMR spectra (Table 1) showed the existence of two oxymethine protons, one vinyl proton, and two secondary methyl groups. These data suggested that compounds **2** and **3** are lupane triterpenes without

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10.1021/np800594a CCC: $40.75
Published on Web 06/03/2009

Table 1. ^{1}H NMR ($CDCl_3$) Data of Triterpenes **1**−**5**[a]

proton	1	2	3	4	5
1		1.61−1.68 m			
2	2.04 m	1.95−2.04 m		2.16 m	
3	3.38 m	3.41 bt (2.7)	3.22 dd (10.2, 4.7)		3.22 t (8.7)
4				1.80−2.00 m	
6					5.32 d (2.9)
7		1.95−2.04 m	1.80−2.10 m		3.86 dd (8.7, 2.9)
8					1.57−1.67 m
11		1.95−2.04 m	1.80−2.10 m	1.80−2.00 m	
12		5.20 t (3.4)	5.18 t (3.3)		
13	1.86 m				
15	2.18 m				
16	3.82 dd (11.5, 4.2)	4.22 dd (11.5, 5.3)	4.22 dd (11.5, 5.3)	3.61 dd (11.1, 4.7)	
19	2.42 m			2.51 m	
22		1.61−1.68 m			2.00 m
23	0.95 s	0.96 s	0.79 s	0.90 d (6.8)	0.79 s
24	0.82 s	0.84 s	0.99 s	0.90 d (6.8)	0.99 s
25	0.84 s	0.96 s	0.79 s	0.81 s	3.59 m 3.36 t (7.5)
26	1.00 s	1.02 s	1.02 s	1.05 s	1.14 s
27	1.05 s	1.16 s	1.14 s	0.98 s	1.05 s
28	4.16 d (11.2)	0.77 s	0.76 s	0.79 s	1.03 s
29	4.69 s	0.95 d (8.6)	0.94 d (7.4)	4.70 s	0.91 s
	4.60 s			4.60 s	
30	1.68 s	0.78 d (7.8)	0.94 d (7.4)	1.68 s	0.79 s

[a] *J* values (in hertz) in parentheses.

Table 2. ^{13}C NMR ($CDCl_3$) Data of Triterpenes **1**−**5**[a]

carbon	1	2	3	4	5	carbon	1	2	3	4	5
1	33.3 t	35.0 t	38.5 t	32.9 t	18.0 t	16	79.7 d	66.9 d	66.9 d	76.5 d	33.2 t
2	25.3 t	25.0 t	27.0 t	29.9 t	27.8 t	17	51.4 s	38.1 s	48.8 s	44.4 s	38.8 s
3	76.2 d	75.9 d	78.8 d	179.0 s	78.5 d	18	48.0 d	60.5 d	60.5 d	47.6 d	54.9 d
4	37.5 s	37.1 s	39.7 s	25.4 d	41.9 s	19	47.6 d	39.3 d	39.3 d	47.5 d	33.2 t
5	49.0 d	48.7 d	54.9 d	40.5 d	142.7 s	20	149.6 s	39.3 d	39.3 d	149.8 s	32.0 s
6	18.2 t	18.0 t	18.1 t	18.2 t	124.5 d	21	29.6 t	30.1 t	30.3 t	28.2 t	31.0 t
7	34.1 t	35.8 t	35.0 t	32.8 t	75.1 d	22	32.1 t	32.5 t	32.5 t	37.7 t	39.3 t
8	41.2 s	40.1 s	40.1 s	40.7 s	52.3 d	23	28.2 q	28.0 q	27.9 q	18.8 q	28.0 q
9	49.6 d	46.5 d	46.7 d	47.3 d	38.5 s	24	22.1 q	22.1 q	15.4 q	19.5 q	15.3 q
10	37.2 s	36.6 s	36.6 s	39.9 s	58.3 d	25	15.9 q	15.3 q	17.4 q	24.7 q	62.3 t
11	20.6 t	23.0 t	23.1 t	29.7 t	27.3 t	26	16.1 q	16.6 q	16.6 q	16.0 q	22.3 t
12	24.9 t	124.9 d	124.9 d	24.8 t	26.6 t	27	16.0 q	24.4 q	24.3 t	15.9 q	16.8 q
13	36.6 d	137.7 s	137.7 s	37.3 d	42.7 s	28	61.2 t	21.7 q	21.7 q	11.7 q	17.1 q
14	44.7 s	43.9 s	43.8 s	48.6 s	46.7 s	29	110.0 t	21.1 q	15.5 q	109.9 t	21.1 q
15	29.3 t	33.0 t	36.3 t	36.9 t	41.5 t	30	19.2 q	17.3 q	21.1 q	19.3 q	28.5 q

[a] Data based on DEPT, HSQC, and HMBC experiments.

the C-20−C-29 double bond.[11] Their ^{13}C NMR spectra also confirmed the presence of a trisubstituted double bond and the existence of two oxymethine carbons. The location of the C-12−C-13 double bond and also the positions of the C-3 and C-16 hydroxy groups were established on the basis of the following HMBC correlations: H-16/C-22, H-16/C-15, H-16/C-14, H-12/C-18, H-12/C-9, H-12/C-14, H-3/C-23, H-3/C-24.

The main difference between **2** and **3** is the orientation of the C-3 hydroxy group. The H-3 resonance of **2** at δ 3.41 (bt, $J = 2.7$ Hz, 1H) represents a β-oriented proton, on the basis of the coupling constants and confirmed by a ROESY experiment showing NOE effects with Me-23 and Me-24 (δ 0.96, 0.85). In the case of **3**, the orientation of H-3 was opposite of that observed in **2**. The H-3 resonance of **3** at δ 3.22 (dd, $J = 10.2$, 4.7 Hz, 1H) represents an α-oriented proton, from the coupling constant values and because only an NOE effect between H-3 and Me-23 was detected. These data allowed us to define the structure of compound **2** as 3α,16β-dihydroxylup-12-ene, and the structure 3β,16β-dihydroxylup-12-ene for compound **3**.

Compound **4** was isolated as an amorphous, white solid with the molecular formula $C_{30}H_{50}O_3$ assigned by HRMS. Its IR spectrum showed absorption bands for hydroxy groups (3436 cm^{-1}) and a terminal double bond (1644 cm^{-1}). The^{1}H NMR spectrum (Table 1) showed four methyl groups [δ 1.05, 0.98, 0.81, 0.79], an isopropenyl group [δ 1.68 (3H, s, H-30), 4.70 (1H, s, H-29a), and 4.60 (1H, s, H-29b)], one oxymethine proton [δ 3.61 (1H, dd, $J =$ 11.1, 4.7 Hz, H-16)], and the typical lupane H$_\beta$-19 proton at δ 2.51 (1H, m). As in the case of **2** and **3**, this compound showed also two methyl doublets at δ 0.90 (6H, d, $J = 6.8$ Hz, H-23, H-24).

Its ^{13}C NMR and DEPT spectra (Table 2) revealed the presence of seven methyl groups and 10 methylene, seven methine, and six quaternary carbons. The $\Delta^{20,29}$ functionality of a lupane triterpene was again confirmed by the presence of the two sp^2 carbons at δ 149.8 (s) and 109.9 (t). A carbonyl carbon at δ 179.0 and an oxymethine carbon at δ 76.5 were also detected. Compound **4** has six degrees of unsaturation. One is due to the terminal isopropenyl group, another one corresponds to the carboxylic acid carbon, and the remaining four unsaturations could be the result of rings. The existence of three oxygen atoms in its structure, the presence of two methyl doublets, and the existence of four rings suggested that compound **4** was a secolupane triterpene[12−14] with a carboxyl group at C-3.

The hydroxy group was located at C-16, due to HMBC correlations of H-16/C-28 and H-16/C-22. The orientation of the C-16 hydroxy group was assigned as α since an NOE effect between H-16 and Me-27 was detected. All these data, when compared with those for other secolupane triterpenes such as 3,4-secolup-20(29)-en-3-oic acid,[12] its methyl ester,[13] and canaric acid,[14] allowed us to establish the structure of compound **4** as 16β-3,4-secolup-20-(29)-en-3-oic acid.

Compound **5** was isolated as an amorphous solid with the molecular formula $C_{30}H_{48}O_3$ assigned by HRMS. Its IR spectrum revealed absorption bands for hydroxy groups (3454 cm^{-1}). The ^1H NMR spectrum (Table 1) showed signals for seven methyl groups (δ 0.79 (×2), 0.91, 0.99, 1.03, 1.05, 1.14), none of them attributable to the methyl group of the typical isopropenyl moiety of the lupane skeleton. In addition, the ^1H NMR spectrum shows two oxymethine protons [δ 3.22 (1H, t, J = 8.7 Hz, H-3), 3.86 (1H, dd, J = 8.7, 2.9 Hz, H-7)] and two oxymethylene protons [δ 3.59 (1H, m, H-25a), 3.36 (1H, t, J = 7.5 Hz, H-25b)]. Its ^{13}C NMR and DEPT spectra (Table 2) revealed the existence of 30 carbons. The presence of a trisubstituted double bond was confirmed by the quaternary carbon at δ 142.7 and the methine carbon at δ 124.5. The spectra also showed three oxygenated carbons at δ 78.5, 75.1, and 62.3. The molecular formula indicated seven degrees of unsaturation, one attributable to the vinyl moiety and the other six corresponded to rings. Compound **5** exhibited typical characteristics of a glutinane pentacyclic triterpene;[15] consequently, the additional ring must be an oxygen heterocycle. The presence of three oxygen atoms in the molecular formula, the possible existence of an oxygenated heterocyclic ring, and the absence of carbonyl moiety suggested that **5** contains a hydroperoxy group.

The hydroperoxy group was assigned at C-3 from the HMBC correlations between the proton at δ 3.22 and two methyl groups at δ 28.0 and 15.3. The location of the double bond between carbons C-5 and C-6 and the cyclic ether between carbons C-25 and C-7 were also established from the following HMBC correlations: H-6/C-4, H-6/C-10, H-6/C-8, H-6/C-25, H-7/C-8, H-7/C-25. All these data established the final structure of compound **5** as 3β-hydroperoxy-7β,25-epoxy-D:B-friedoolean-5-ene.

Compound **6** showed a molecular formula of $C_{34}H_{34}O_8$, established by HRMS. The IR spectrum showed signals for ether (1454, 1374 cm^{-1}) and ester (1714 cm^{-1}) groups. Its ^1H NMR spectrum showed signals for two monosubstituted aromatic rings and also for two 1,3,4-trisubstituted aryl groups [δ 6.79 (2H, dd, J = 8.0, 1.8 Hz), 6.61 (2H, dd, J = 8.0, 1.8 Hz), 6.53 (2H, d, J = 1.8 Hz)]. In addition to aromatic protons, signals corresponding to two oxymethylene groups [δ 4.54 (2H, dd, J = 11.2, 5.9 Hz), 4.35 (2H, dd, J = 11.2, 4.3 Hz)] and two methoxy groups at δ 3.77 (6H, s) were also detected. Finally, the ^1H spectrum showed the presence of aliphatic protons characteristic of dibenzylbutane lignans.[16] Its ^{13}C NMR spectrum showed signals for 15 carbons. The most significant signals were an ester carbonyl carbon at δ 166.5 (s), two methylene carbons (δ 65.0, 35.1), and a methine carbon at δ 40.4. The remaining signals correspond to aromatic carbons.

The molecular formula indicated the presence of 34 carbons, and the data from the ^1H NMR and ^{13}C NMR spectra suggested that this compound is symmetric. The analysis of the fragments observed in the mass spectrum confirmed this conjecture [(570, $M^{+\bullet}$), (325, $[M^{+\bullet} - 1] - (2 \times C_7H_6O_2)$, (137, $C_8H_9O_2$)]. Compound **6** showed a negative specific rotation ($[\alpha]_D^{20}$ −20, c 0.45, $CHCl_3$), and therefore its absolute configuration is either 8*R*, 8′*R* or 8*S*, 8′*S,* because the other two possibilities correspond to optically inactive meso structures.

Taking these data into account, the structure of compound **6** is 9,9′-dibenzoylsecoisolariciresinol.[17]

Because of the demonstrated anti-HIV activity[18,19] of lupane triterpenes, the new compounds were tested for antifusogenic activity. However, none of them showed significant activity.

Experimental Section

General Experimental Procedures. Optical rotations were measure with a Perkin-Elmer 241 automatic polarimeter. UV spectra were recorded in absolute EtOH on a JASCO V-560 spectrophotometer. IR spectra were obtained using a Bruker IFS28/55 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively, with TMS as the internal reference. 2D NMR experiments were conducted on a Bruker WP-400 SY NMR spectrophotometer in $CDCl_3$ at 400 MHz. High- and low-resolution mass spectra were obteined on a VG Autospec spectometer. Macherey-Nagel polygram Sil G/UV_{254} and preparative TLC sil G-100UV254 foils were used for TLC. Silica gel (0.2−0.63 mm) and Sephadex LH-20 (Biosigma) were used for column chromatography.

Plant Material. Leaves of *M. apurimacensis* were collected at Huayllabamba (Peru), in November 2001, and were identified by the botanist G. Yarupaitan. A voucher specimen is on file (No. 2650) at the Herbarium of San Marcos (USM).

Extraction and Isolation. Dried leaves of *M. apurimacensis* (1 kg) were extracted with EtOH in a Soxhlet apparatus. Evaporation of the solvent under reduced pressure provided 263.5 g of a dark extract. This residue was chromatographed on silica gel eluted with mixtures of *n*-hexane/EtOAc of increasing polarity. Eight fractions, A−H, were separated and further chromatographed on Sephadex LH-20 and Si gel using as solvents mixtures of *n*-hexane/$CHCl_3$/MeOH (2:1:1) and *n*-hexane/EtOAc, respectively. Some of the eluted products were separated by preparative TLC. Compounds **2** (18 mg), **3** (28 mg), **5** (4.5 mg), and resinone[7] (45 mg) were isolated from fraction C. Compound **4** (19 mg), calenduladiol[5] (26 mg), resinone[7] (28 mg), and 3-epicalenduladiol[6] (14 mg) were isolated from fraction D. Fraction E yielded loliolide[9] (23 mg), **1** (6 mg), vierol[8] (5.5 mg), divanillyltetrahydrofuran[10] (54 mg), and **6** (5 mg).

3α,16β,28-Trihydroxylup-20(29)-ene (1): amorphous, white solid; $[\alpha]^{20}_D$ +2.5 (c 0.56, $CHCl_3$); UV (EtOH) λ_{max} (log ε) 329 (1.99); 283 (2.54) nm; IR (film) γ_{max} 3369, 2924, 2855, 2360.8, 2342.0, 1720, 1459, 1028, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (see Table 1); ^{13}C NMR ($CDCl_3$, 75 MHz) (see Table 2); EIMS m/z (rel int) 458 ($M^{+\bullet}$, 3), 440 (60), 422 (33), 201 (61), 189 (96); HREIMS 458.3771 (calcd for 458.3759, $C_{30}H_{50}O_3$).

3α,16β-Dihydroxylup-12-ene (2): amorphous, white solid; $[\alpha]^{20}_D$ +16.87 (c 0.48; $CHCl_3$); UV (EtOH) λ_{max} (log ε) 276 (2.11) nm; IR (film) γ_{max} 3406, 2925, 2855, 2361, 1728, 1456, 1380, 1056, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (see Table 1); ^{13}C NMR ($CDCl_3$, 75 MHz) (see Table 2); EIMS m/z (rel int) 442 ($M^{+\bullet}$, 12), 424 (20), 409 (3), 235 (18), 219 (16); HREIMS 442.3839 (calcd for 442.3811, $C_{30}H_{50}O_2$).

3β,16β-Dihydroxylup-12-ene (3): amorphous, white solid; $[\alpha]^{20}_D$ +34.84 (c 0.66; $CHCl_3$); UV (EtOH) λ_{max} (log ε) 202 (3.4) nm; IR (film) γ_{max} 3387, 2926, 2856, 1729, 1457, 1380, 1048, 1029, 997, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (see Table 1); ^{13}C NMR ($CDCl_3$, 75 MHz) (see Table 2); EIMS m/z (rel int) 442 ($M^{+\bullet}$, 12), 424 (7), 409 (2), 235 (20), 219 (27); HREIMS 442.3806 (calcd for 442.3811, $C_{30}H_{50}O_2$).

16β-3,4-Secolup-20(29)-en-3-oic acid (4): amorphous, white solid; $[\alpha]^{20}_D$ +13.03 (c 0.3; $CHCl_3$); UV (EtOH) λ_{max} (log ε) 276 (0.53) nm; IR (film) γ_{max} 3436, 2927, 2859, 1711, 1644, 1461, 1382, 1218, 1020, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (see Table 1); ^{13}C NMR ($CDCl_3$, 75 MHz) (see Table 2); EIMS m/z (rel int) 458 ($M^{+\bullet}$, 20), 443 (4), 425 (17), 397 (13); HREIMS 458.3766 (calcd for 458.3760, $C_{30}H_{50}O_3$).

3β-Peroxy-7β,25-epoxy-D:B-friedoolean-5-ene (5): amorphous solid; $[\alpha]^{20}_D$ +5.33 (c 0.5; $CHCl_3$); UV (EtOH) λ_{max} (log ε) 203 (0.80) nm; IR (film) γ_{max} 3454, 2925, 2855, 1729, 1459, 1382, 1074, 997 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (see Table 1); ^{13}C NMR ($CDCl_3$, 75 MHz) (see Table 2); EIMS m/z (rel int) 456 ($M^{+\bullet}$, 6), 426 (10), 425 (33), 409 (12), 391 (7); HREIMS 456.3632 (calcd for 456.3603, $C_{30}H_{48}O_3$).

9,9′-Dibenzoylsecoisolariciresinol (6): amorphous, orange solid; $[\alpha]^{20}_D$ −20.2 (c 0.5, $CHCl_3$); UV (EtOH) λ_{max} (log ε) 281.2 (3.7), 229.4 (4.3) nm; IR (film) γ_{max} 2923, 2853, 2360, 2338, 1714, 1603, 1514, 1454, 1374, 1270, 1115, 1031, 756, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ_H 8.01 (4H, d J = 8.0 Hz, H-13, H-13′, H-17, H-17′), 7.57 (2H, t, J = 6.5 Hz, H-15, H-15′), 7.43 (4H, t, J = 7.7 Hz, H-14, H-14′; H-16, H-16′), 6.79 (2H, dd, J = 8.0, 1.8 Hz, H-5, H-5′), 6.61 (2H, dd, J = 8.0, 1.8 Hz, H-6, H-6′), 6.53 (2H, d, J = 1.8 Hz, H-2, H-2′), 5.45 (2H, s, OH), 4.54 (2H, dd, J = 11.2, 5.9 Hz, H-9a, H-9′a), 4.35 (2H, dd, J = 11.2, 4.3 Hz, H-9b, H-9′b), 3.77 (6H, s, H-10, H-10′), 2.81 (4H, m, H-7, H-7′), 2.36, (2H, m, H-8, H-8′); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 166.5 (s, C-11, C-11′), 146.5 (s, C-3, C-3′), 144.0 (s, C-4, C-4′), 133.0 (d, C-15, C-15′), 131.5 (s, C-1, C-1′), 130.1 (s, C-12, C-12′), 129.5 (d, C-13, C-13′; C-17, C-17′), 128.4 (d, C-14, C-14′; C-16, C-16′), 121.7 (d, C-6, C-6′), 114.2 (d, C-5, C-5′), 111.2 (d, C-2, C-2′), 65.0 (t, C-9, C-9′), 55.6 (c, C-10, C-10′), 40.4 (d, C-8, C-8′), 35.1 (t, C-7, C-7′); EIMS m/z (rel int) 570 [$M^{+\bullet}$] (82), 448 (6), 425

(33), 326 (18) 137 (100); HREIMS 570.2240 (calcd for $C_{34}H_{34}O_8$, 570.2254), 325.1459 (calcd for $M^{+\bullet} - 1 - (2 \times C_7H_6O_2)$, 325.1440), 137.0599 (calcd for $C_8H_9O_2$, 137.0603).

Acknowledgment. This work has been partly funded by the Spanish MEC (SAF 2006-06720) and by the ICIC (Instituto Canario de Investigación del Cáncer). N.J.V. thanks Gobierno Autónomo de Canarias for a predoctoral fellowship.

Supporting Information Available: Figures showing selected HMBC and ROESY correlations for compounds **1** and **5**. Scheme showing the possible biogenetic relationships between the isolated lupanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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NP800594A