16-Hydroxylated Withanolides from *Exodeconus maritimus*

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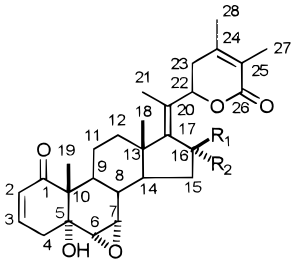
In addition to the known compounds withanolide A (**4**), withanone (**5**), and NIC-3 (**6**), three 16-hydroxylated withanolides were isolated from *Exodeconus maritimus*. The new withanolides were identified as 6α,7α-epoxy-5α,16*β*-dihydroxy-1-oxowitha-2,17(20),24-trienolide (exodeconolide A, **1**), 6α,7α-epoxy-5α,16α-dihydroxy-1-oxowitha-2,17(20),24-trienolide (exodeconolide B, **2**), and 6α,7α-epoxy-5α,16α,17α-trihydroxy-1-oxowitha-2, 24-dienolide (exodeconolide C, **3**), by a combination of spectroscopic (1D and 2D NMR, MS) and chemical methods with the aid of molecular modeling.

Exodeconus Raf. is a genus in the Solanaceae represented by six species that grow in Perú, mainland Ecuador, and on the Galapagos Islands.[1] Thus far, none of the species of this genus has been subjected to a phytochemical study. As part of a program aimed at the discovery of novel withanolides from species of the Solanaceae, we report the isolation of the new withanolides exodeconolides A−C (**1**−**3)** along with the known withanolide A[2] (**4**), withanone[3] (**5**), and NIC-3[4] (**6**) from *Exodeconus maritimus* (Benth.) D'Arcy. This report of withanolides in *Exodeconus* may be important from the chemotaxonomic point of view, on account of the different opinions that have been expresed concerning its systematic position at the tribal level (Hunziker, A. T., personal communication). It is noteworthy that no alkaloids were detected in this species. On the other hand, many of the previously reported withanolides possess biological activity, such as antimicrobial, antitumor, antiinflammatory, hepatoprotective, immunomodulatory, and insect-antifeedant properties.[5] In addition, a recent investigation has reported withanolides as ecdysteroid antagonists related to chemical-defense mechanisms.[6]

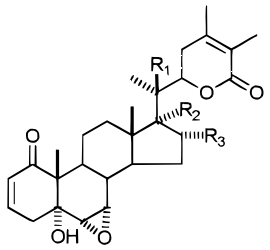
The identity of the new compounds was determined using a combinations of spectroscopic data including 2D-NMR techniques, molecular modeling, and chemical transformations.

Results and Discussion

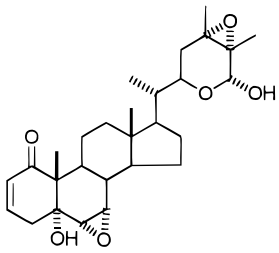
Exodeconolide A (**1**) revealed a molecular formula of $C_{28}H_{36}O_6$ by mass spectrometry. The FABMS (*m*-nitrobenzyl alcohol, KCl) showed a quasimolecular ion at *m*/*z* 507 corresponding to the $[M + K]^+$ ion; the HREIMS failed to show a molecular ion, but exhibited a $[M - H_2O]^+$ ion at *m*/*z* 450.2407 (calcd for $C_{28}H_{34}O_5$, 450.2406). The EIMS also showed an ion at *m*/*z* 125, which may be assigned to the α,*β*-unsaturated-*δ*-lactone ring ($C_7H_9O_2$) upon cleavage between C-20 and C-22.



1: R_1 = OH, R_2 = H
2: R_1 = H, R_2 = OH
7: R_1,R_2 = O
8: R_1 = OAc, R_2 = H



3: R_1 = H, R_2 = R_3 = OH
4: R_1 = OH, R_2 = R_3 = H
5: R_1 = R_3 = H, R_2 = OH



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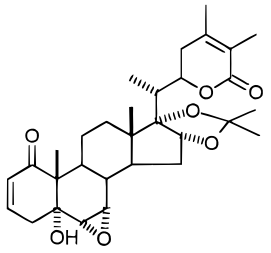

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The ^{1}H-NMR spectrum of **1** (Table 1) showed the characteristic signals of a 1-oxo-2,3-ene-5α-hydroxy-6α,7α-epoxywithanolide for the A- and B-ring substitution pattern.[5] Thus, signals with the expected multiplicities were observed at *δ* 6.60 and 5.85 for the olefinic protons and at *δ* 3.33 and 3.06 for the epoxide protons. The presence of an α,*β*-unsaturated-*δ*-lactone ring was confirmed by the two methyl signals at *δ* 1.90 and 1.95, corresponding to the C- 27 and C-28 methyls, respectively. The H-22 signal appeared at *δ* 5.52 (dd, *J* = 13.2, 3.7 Hz) and showed cross-correlation peaks in the COSY spectrum only with the H-23 signals at *δ* 2.71 and 2.02. The latter signals were only partially visible in the 1D spectrum due to overlapping with neighboring multiplets; however, their multiplicities and approximate couplings could be measured in the COSY spectrum from the cross peaks with H-22, in spite of the lower resolution. The axial H-23 signal also showed a cross

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Table 1. ^{1}H- and ^{13}C-NMR Data of Exodeconolide A (**1**) from 1D and 2D NMR Experiments[a]

	δ_H				δ_H		
carbon	α	β	δ_C	carbon	α	β	δ_C
1			202.9	15	1.49 m	2.35 m	34.2
2	5.85 ddd (10.1; 2.8; 1.0)		128.9	16	4.72 br t (7.1)		72.0
3	6.60 ddd (10.1; 5.0; 2.4)		139.7	17			153.1
4	2.52 ddd (19.0; 5.0; 1.0)	2.68 ddd (19.0; 2.8; 2.4)	36.7	18	1.13 s		17.1
5			73.2	19	1.19 s		14.6
6		3.06 d (3.8)	56.3	20			127.5
7		3.33 dd (3.8;1.8)	56.8	21	1.82 d (1.3)		12.8
8		1.86 m	35.0	22	5.52 dd (13.2; 3.7)		76.7
9	1.58 m		35.4	23	2.02 dd[b] (18; 3.7)	2.71 br dd[c] (13.2; 18)	33.7
10			51.0	24			149.2
11	2.83 dq (13.1; 3.1)	1.39 m	21.9	25			122.0
12	1.60 m	2.26 m	37.3	26			166.7
13			45.0	27	1.90 d (1.0)		12.5
14	1.40 m		47.1	28	1.95 br s		20.3

[a] Chemical shifts in ppm downfield from TMS. *J* couplings (in parentheses) in Hz. ^{1}H- and ^{13}C-NMR spectra measured in $CDCl_3$ at 200.13 and 50.32 MHz, respectively. [b] Equatorial. [c] Axial.

peak with the 27-methyl (δ 1.90), which appeared as a 1 Hz doublet in the 1D spectrum.

The multiplicity of H-22 (double doublet) indicated the absence of protons attached to C-20. Although in withanolides this typically indicates a 20-hydroxylated compound,[5] the high chemical shifts of H-22 and of the 21-methyl signal (δ 1.82) suggested the presence of a C-17, C-20 double bond.[7] Finally, a broad triplet was present at δ 4.72, indicating an additional oxygenated substituent; a small coupling interaction was detected between this signal and the methyl at C-20 (d, $J = 1.3$ Hz), both through a cross peak in the COSY spectrum and by selective irradiation of the δ 4.72 signal, suggesting a homoallylic relationship between these hydrogens. Thus, the δ 4.72 signal was assigned to H-16 of a C-16-hydroxylated withanolide.

The ^{13}C-NMR spectrum of exodeconolide A (Table 1) exhibited 28 signals that, according to the DEPT spectrum, corresponded to five methyls, five methylenes, nine methines, and nine quaternary carbons. Apart from the signals corresponding to the characteristic substitution of the A and B rings and those corresponding to the δ-lactone moiety, the ^{13}C-NMR spectrum revealed the oxygenated carbon signal corresponding to C-16 at δ 72.0, which correlated with the proton signal at δ 4.72 (assigned to H-16) in the HETCOR spectrum. An extra tetrasubstituted double bond was inferred from the quaternary carbon signals at δ 153.1 and δ 127.5, assigned to C-17 and C-20, respectively. The remaining proton and carbon resonances (see Table 1) were assigned based on the COSY and HETCOR spectra.

The β-orientation of the C-16-hydroxyl group was determined by the combined analysis of the coupling constants involving H-15α, H-15β, and H-16, the NOESY spectrum, and molecular modeling of both α and β-epimers at C-16. The most stable rotamer around the C-20−C-22 bond of each epimer was obtained using AM1 calculations, and the vicinal coupling constants involving H-15α, H-15β, and H-16 were calculated using the Altona equation.[8] For the 16β-hydroxy epimer the predicted values were $J_{15\alpha,16\alpha} = 9.40$ Hz and $J_{15\beta,16\alpha} = 6.20$ Hz, while for the 16α-hydroxy epimer the calculated values were 1.29 and 7.65 Hz, respectively. The observed multiplicity of H-16 in **1** (broad triplet, $J = 7.1$ Hz) is in fair agreement with the values calculated for the 16β-hydroxy isomer.

Table 2. Relevant NOE Correlations in the NOESY Spectrum of Exodeconolide A (**1**) ($CDCl_3$, 200.13 MHz)[a]

	1	
proton(s)	δ	correlates with δ[b]
4α	2.52	3.06 (H-6, 2.6 Å)
4β	2.68	3.06 (H-6, 2.5 Å)
7β	3.33	2.35 (H-15β, 2.6 Å)
8β	1.86	1.19 (H-19, 2.2 Å) 1.13 (H-18, 2.1 Å)
11β	1.39	1.19 (H-19, 2.1 Å)
12β	2.26	1.82 (H-21, 2.2 Å)
16α	4.72	5.52 (H-22, 2.4 Å)
18	1.13	1.82 (H-21, 2.3 Å)

[a] Interactions between vicinal and geminal hydrogens are not included. [b] Distances between interacting hydrogens from AM1 calculations are given in parentheses.

The relevant correlations in the NOESY spectrum of exodeconolide A are presented in Table 2, together with the distances between the interacting hydrogens in the AM1-optimized geometry. The absence of a NOE correlation between H-16 and the C-18 methyl, supported the proposed stereochemistry at C-16; this was confirmed by the observation of a NOE cross peak between these hydrogens in the C-16α-hydroxy analogue (see below). A strong correlation between H-16 and H-22 and weaker ones for the pairs methyl-18/methyl-21 and H-12β/methyl-21 allowed unequivocal assignment of the *Z* stereochemistry to the C-17, C-20 double bond. Figure 1 shows a partial 3D view of the most stable rotamer of **1**, where the arrows indicate the relevant observed NOEs.

The oxidation of the allylic alcohol at C-16 with MnO_2 to the α,β-unsaturated ketone (**7**) confirmed the presence of the C-17, C-20 double bond. As expected, the signals corresponding to methyl-21 and H-22 in com-

Table 3. ^{1}H-NMR Data of Compounds **2**, **3**, **7**, **8,** and **9** ($CDCl_3$, 200.13 MHz)[a]

proton(s)	**2**	**3**	**7**	**8**	**9**
2	5.85 dd (10.2; 2.2)	5.84 dd (10.1; 2.1)	5.87 dd (10.1; 1.8)	5.85 dd (10.1; 2.0)	5.85 dd (10.0; 2.6)
3	6.60 ddd (10.2; 5.1; 2.5)	6.58 ddd (10.1; 4.8; 2.3)	6.61 ddd (10.1; 5.0; 2.5)	6.60 ddd (10.1; 4.9; 2.3)	6.59 ddd (10.0; 4.8; 2.6)
4α	2.53 dd (18.7; 5.1)	2.55 dd (18.7; 4.8)			
4*β*	2.70 ddd (18.7; 2.5; 2.2)	2.70 ddd (18.7; 2.3; 2.1)			
6	3.07 d (3.9)	3.03 d (3.9)	3.08 d (3.9)	3.05 d (3.9)	3.04 d (3.9)
7	3.33 dd (3.9; 1.8)	3.24 dd (3.9; 1.8)	3.28 dd (3.9; 1.9)	3.29 dd (3.7; 2.1)	3.34 dd (3.9; 2.3)
11α	2.86 dq (13.8; 2.6)	2.78 dq (13.9; 2.8)	2.96 dq (14.0; 3.1)	2.86 dq (13.1; 2.6)	
16	4.75 br d (4.3)	4.38 dd[b] (9.4; 2.0)		5.69 br t (6.1)	5.17 br d (7.5)
18	0.95 s	0.87 s	1.17 s	1.12 s	0.90 s
19	1.19 s	1.16 s	1.21 s	1.19 s	1.19 s
20		2.20 dq (6.9; 5.6)			
21	1.84 s	1.05 d (6.9)	2.04 s	1.83 d (1.0)	0.98 d (7.4)
22	5.37 dd (12.7; 3.7)	4.61 ddd (11.6; 5.6; 4.6)	6.53 dd (12.3; 3.6)	4.90 dd (12.9; 3.4)	4.65 m
23eq	2.18 dd (17.1; 3.6)	2.41 m			
23ax	2.67 dd (17.1; 12.7)	2.41 m			
27	1.90 br s	1.87 br s	1.90 br s	1.88 br s	1.88 br s
28	1.94 br s	1.94 br s	1.94 br s	1.94 br s	1.94 br s
				2.04 s (AcO)	1.50 s, 1.34 s (Me)

[a] Chemical shifts are in ppm downfield from TMS; *J* couplings (in parentheses) in Hz. [b] After exchange with D_2O.

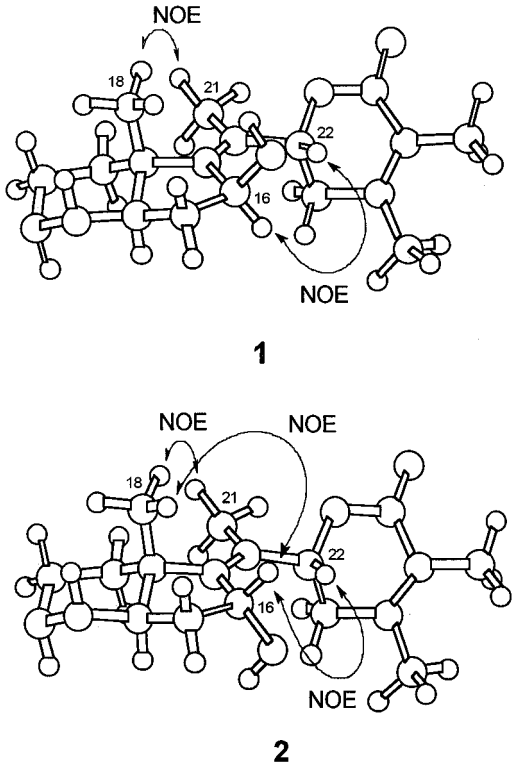

Figure 1. Partial view of the most stable conformers of exodeconolides A (**1**) and B (**2**) from AM1 calculations, showing NOE interactions relevant to stereochemistry of 16-hydroxyl and 17,20 double bond (see Tables 2 and 5).

pound **7** were shifted downfield with respect to exodeconolide A, resonating at *δ* 2.04 and *δ* 6.53, respectively (Table 3). The ^{13}C-NMR spectrum of **7** (Table 4) confirmed the formation of the ketone at C-16 (carbonyl at *δ* 204.9) and showed the concomitant downfield shift of C-20 to *δ* 146.5 (+ 19 ppm compared to compound **1**) due to conjugation with the carbonyl group.

Table 4. ^{13}C-NMR Data of Compounds **2**, **3**, **7**, and **8** ($CDCl_3$, 50.32 MHz)

carbon	**2**	**3**	**7**	**8**
1	203.3	203.0	202.7	202.9
2	128.9	129.0	129.0	129.0
3	139.8	139.6	139.8	139.7
4	36.8	36.7	36.7	36.7
5	73.4	73.2	73.2	73.2
6	56.3	56.2	56.2	56.3
7	56.9	57.0	56.7	56.7
8	35.0	35.0	34.6	35.2
9	35.5	35.7	35.4	35.4
10	51.1	50.9	51.0	50.9
11	22.0	21.4	22.1	22.0
12	37.5	33.2[a]	37.1	37.4
13	45.3	49.6	45.2	45.1
14	48.3	44.1	45.7	47.5
15	34.7	34.7	39.2	31.9
16	71.7	75.6	204.9	76.6
17	150.3	82.2	142.1	147.3
18	16.9	14.8[b]	17.2	16.4
19	14.7	14.7[b]	14.7	14.6
20	130.1	43.3	146.5	128.5
21	12.2	10.5	13.5	12.9
22	77.6	77.8	73.8	72.8
23	34.6	33.9[a]	34.5	33.8
24	150.1	150.6	149.0	149.3
25	125.1	121.2	121.9	121.8
26	166.7	167.0	166.2	166.6
27	12.5	12.2	12.5	12.5
28	20.3	20.6	20.2	20.3
Ac				171.2, 21.2

[a,b] Assignments with the same superscript are interchangeable.

Acetylation of **1** yielded the monoacetylated derivative **8**. In the ^{1}H-NMR spectrum acetylation produced, besides the expected downfield shift of the H-16 signal (to *δ* 5.69), an upfield shift of the H-22 signal (to *δ* 4.90). The latter probably originates on rotation of the side-

Table 5. Relevant NOE Correlations Observed in the NOESY Spectra of Exodeconolides B (**2**) and C (**3**) ($CDCl_3$, 200.13 MHz)[a]

	2		**3**	
proton(s)	δ	correlates with δ[b]	δ	correlates with δ[b]
4α	2.53	3.07 (H-6, 2.6 Å)	2.55	3.03 (H-6, 2.6 Å)
16β	4.75	5.37 (H-22, 2.3 Å)	4.38	4.61 (H-22, 2.1 Å)
		0.95 (H-18, 2.9 Å)		0.87 (H-18, 2.6 Å)
18	0.95	1.84 (H-21, 2.3 Å)		

[a] Interactions between vicinal and geminal hydrogens are not included. [b] Distances between interacting hydrogens from AM1 calculations are given in parentheses.

chain around the C-20−C-22 bond due to the steric hindrance introduced by the 16-acetate, giving a more stable rotamer with a different spatial position of H-22 relative to the C-17, C-20 double-bond plane.

The ^{13}C-NMR and DEPT spectra (Table 4) of exodeconolide B (**2**) were almost identical to those exhibited by compound **1**. Small differences (ca. 3 ppm or less) were observed in the chemical shifts of C-17, C-20 and other ring D and side-chain carbons. The EIMS of **2** showed the molecular ion at *m/z* 468 ($C_{28}H_{36}O_6$), but due to its low intensity the high-resolution measurement was carried out on the $[M - H_2O]^+$ ion at *m/z* 450.2406 (calcd for $C_{28}H_{34}O_5$, 450.2406). Several additional pieces of evidence suggested that compound **2** was the C-16 epimer of **1**. The ^{1}H-NMR spectrum of **2** (Table 3) showed H-16 as a broad doublet (J = 4.3 Hz) with almost the same chemical shift as in **1**. In the COSY spectrum, H-16 only showed cross-correlation peaks with the H-15 hydrogens at δ 1.65−1.85; other correlations confirmed the assignments made.

The NOESY spectrum of **2** (Table 5) confirmed the α-orientation of the 16-hydroxyl, showing a NOE cross-correlation peak between the methyl at C-13 (H_3-18) and H-16. Correlations were also observed between methyl-18/H-21 and H-16/H-22, thus confirming the *Z* stereochemistry for the C-17, C-20 double bond as in **1**. The ^{1}H-NMR resonance of C-18 methyl showed an upfield shift in **2** (δ 0.95) compared to **1** (δ 1.13), in agreement with the epimeric relationship of the 16-hydroxyl between both compounds. In exodeconolide A (**1**) the 1,3-pseudodiaxial relationship between C-18 methyl group and the 16β-hydroxy group would give rise to the deshielding of the methyl group. Furthermore, the equatorial H-23 resonates at a higher chemical shift in compound **2** (δ 2.18) as compared to **1** (δ 2.02), and this difference may be explained considering that, in its most stable conformation (AM1 calculations), exodeconolide B (**2**) (but not **1**) has the 16-hydroxyl spatially close to the equatorial H-23 (Figure 1).

Exodeconolide C (**3**), $C_{28}H_{38}O_7$ (HREIMS, $[M]^+$ at *m/z* 486.2611, calcd 486.2618), was not found to possess a C-17, C-20 double bond but showed two carbinolic carbon signals at δ 82.2 (C) and 75.6 (CH) in its ^{13}C-NMR spectrum (Table 4). A related 16,17-dihydroxywithanolide with a different substitution pattern in ring B (5β,6β-epoxy) has been isolated from *Discopodium penninervium*.[9] The ^{1}H- and ^{13}C-NMR data of ring D and the side chain of **3** agree well with those reported for the withanolide from *D. penninervium*, while data for rings A and B are closely related to exodeconolides A and B (Tables 3 and 4). In the ^{1}H-NMR spectrum, H-16 was observed as a broad multiplet (δ 4.38) that turned into a double doublet upon exchange with D_2O. The resonances for methyl-21 and H-22 had chemical shifts and multiplicities typical of 17α-hydroxy-20-H withanolides.[10]

The *cis* stereochemistry of the hydroxyls at positions 16 and 17 of exodeconolide C, was confirmed by preparation of the 16,17-acetonide (**9**) (Me_2CO/perchloric acid), and the stereochemistry at C-16 was established from the NOESY spectrum, which showed a NOE cross peak between the C-18 methyl and H-16 (Table 5).

Experimental Section

General Experimental Procedures. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC-200 NMR spectrometer at 200.13 and 50.32 MHz, respectively, in deuteriochloroform solution. Multiplicity determinations (DEPT) and 2D spectra (COSY-45, HETCOR, NOESY) were obtained using standard Bruker software. Chemical shifts are given in parts per million downfield from TMS as internal standard. EIMS were collected on a VG Trio-2 mass spectrometer at 70 eV by direct inlet; FABMS and HREIMS (70 eV) were measured on a VG ZAB-BEQQ mass spectrometer. IR and UV spectra were measured on a Nicolet Magna 560 FTIR and a Hewlett-Packard 8451A spectrophotometer, respectively. AM1 calculations were performed with AMPAC-5.0 (Semichem). Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Column chromatography was performed on Kiesegel 60-G (Merck) or Kieselgel S (0.032−0.063 mm). TLC analysis was performed on Si gel 60 F_{254} (0.2 mm thick).

Plant Material. Whole *E. maritimus* plants were collected in the Department of Trujillo, Perú, during February 1995. A voucher specimen is deposited at Museo Botánico, Universidad Nacional de Córdoba, under no. CORD 25482.

Extraction and Isolation. Dried and pulverized whole plants of *E. maritimus* (560 g) were extracted exhaustively with EtOH and the EtOH extract concentrated at reduced pressure (40 Torr). The residue (104 g) was defatted by partition in hexane−MeOH−H_2O (10:9:1), the MeOH−H_2O phase was washed with hexane (2 × 300 mL), and the MeOH evaporated at reduced pressure (40 Torr). The residue was diluted with H_2O (200 mL) and extracted with $CHCl_3$ (3 × 300 mL). The $CHCl_3$ extract was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness at reduced pressure. The amber residue (25.8 g) obtained after evaporation of the $CHCl_3$ was fractionated by vacuum−liquid chromatography (VLC)[11] eluting with hexane, hexane−C_6H_6 (1:1), C_6H_6, C_6H_6−$CHCl_3$ (1:1), and $CHCl_3$−MeOH mixtures of increasing polarity (100:0, 19:1, 9:1, 4:1, 3:2, 2:3, 0:100). Fractions showing similar TLC behavior were pooled.

The fraction eluting with $CHCl_3$−MeOH 80:20 (11.3 g) was further fractionated by VLC, eluting with hexane−EtOAc−MeOH mixtures of increasing polarity, and the resulting fractions were further processed using a combination of chromatographic techniques including flash chromatography and preparative TLC. This led to the isolation of the known withanolides NIC-3 (**6**) (8 mg), withanolide A (**4**) (85 mg), and withanone (**5**) (65 mg), identified by comparison of their ^{1}H- and ^{13}C-NMR spectra with those described in the literature, and of exodeconolides A (**1**) (125 mg), B (**2**) (12 mg), and C (**3**) (19 mg).

Exodeconolide A (1): white crystals (hexane−EtOAc); mp 260−263 °C; UV (MeOH) λ_{max} 224 nm; IR

(dry film) ν_{max} 3500, 1694, 1687 cm^{-1}; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 1; FABMS (*m*-nitrobenzyl alcohol, KCl) *m/z* $[M + K]^+$ 507 (100), 491 (M − 16 + K, 25), 451 (M + 1 − H_2O, 10); EIMS *m/z* $[M - H_2O]^+$ 450 (3), 435 (4), 357 (2), 343 (2), 299 (3), 152 (side chain, 8), 125 (lactone ring, 20); HREIMS *m/z* found $[M - H_2O]^+$ 450.2407 ($C_{28}H_{34}O_5$ requires 450.2406).

Acetylation with Ac_2O−pyridine (1:1) afforded monoacetate **8**; ^{1}H-NMR data, see Table 3; ^{13}C-NMR data, see Table 4.

Exodeconolide B (2): white crystals (hexane−EtOAc); mp 273−274 °C; UV (MeOH) λ_{max} 227 nm; IR (KBr) ν_{max} 3500, 1695, 1683 cm^{-1}; ^{1}H-NMR data, see Table 3; ^{13}C-NMR data, see Table 4; EIMS *m/z* $[M]^+$ 468 (1), 450 (M − H_2O, 1), 435 (1), 372 (5), 272 (16); HREIMS *m/z* found $[M - H_2O]^+$ 450.2406 ($C_{28}H_{34}O_5$ requires 450.2406).

Exodeconolide C (3): white crystals (hexane−EtOAc); mp 278−279 °C; UV (MeOH) λ_{max} 226 nm; IR (KBr) ν_{max} 3450, 1700, 1683 cm^{-1}; ^{1}H-NMR data, see Table 3; ^{13}C-NMR data, see Table 4; EIMS *m/z* $[M - H_2O]^+$, 468 (1), 450 (M − 2 H_2O, 1), 435 (1), 355 (2), 315 (2), 251 (6), 225 (13), 154 (side chain, 9), 137 (15), 125 (lactone ring, 56); HREIMS *m/z* found $[M]^+$ 486.2618 ($C_{28}H_{38}O_7$ requires 486.2611).

Oxidation of Exodeconolide A (1). MnO_2 (500 mg) was added to a solution of **1** (20 mg) in Me_2CO (25 mL), and the mixture was stirred at room temperature for 48 h. The solution was filtered and evaporated to dryness. Column chromatography of the residue yielded compound **7** (10 mg). ^{1}H-NMR data, see Table 3; ^{13}C-NMR data, see Table 4.

Acetonide of Exodeconolide C (9). To a solution of **3** (8 mg) in Me_2CO (5 mL) was added 70% perchloric acid (1 drop) and the mixture stirred at room temperature for 5 h, extracted with Et_2O, and the solvent removed. The residue was purified by preparative TLC to yield acetonide **9** (4 mg). ^{1}H-NMR data, see Table 3.

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