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SEVEN NEW TRITERPENES FROM *GANODERMA LUCIDUM*

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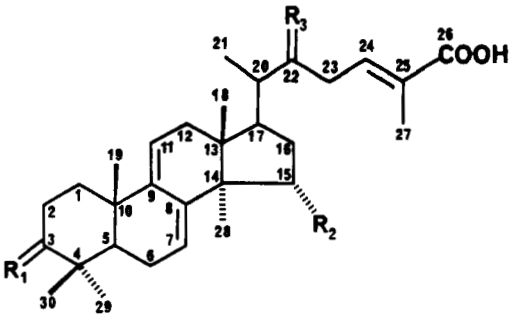
ABSTRACT.—Seven new lanostane-type triterpenes were isolated from the mycelia of *Ganoderma lucidum*. By spectroscopic analysis, their structures were determined to be 3α,15α,22α-trihydroxylanosta-7,9(11),24-trien-26-oic acid [**1**], 3β,15α,22β-trihydroxylanosta-7,9(11),24-trien-26-oic acid [**2**], 3α,15α-diacetoxy-22α-hydroxylanosta-7,9(11),24-trien-26-oic acid [**3**], 3β,15α-diacetoxy-22α-hydroxylanosta-7,9(11),24-trien-26-oic acid [**4**], 22β-acetoxy-3α,15α-dihydroxylanosta-7,9(11),24-trien-26-oic acid [**5**], 22β-acetoxy-3β,15α-dihydroxylanosta-7,9(11),24-trien-26-oic acid [**6**], and 3β,15α-diacetoxylanosta-8,24-dien-26-oic acid [**11**].

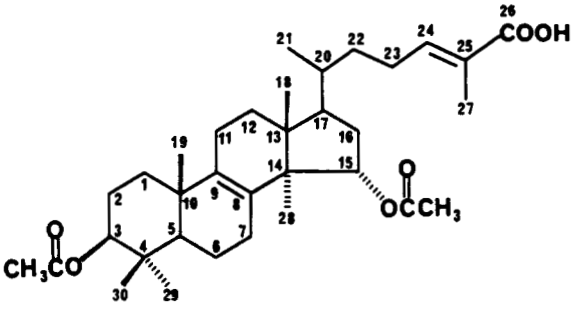
The fungus *Ganoderma lucidum* (Fr.) Karst (Polyporaceae) has long been used in traditional Chinese medicine and has attracted recent attention owing to its production of many biologically active triterpenes (1–5). More than 80 new oxygenated triterpenoids have been isolated to date (1,2, 4–20). Previously, we have reported the isolation of 17 lanostane-type triterpenes including five pairs of stereoisomers (21–23). The subsequent investigation of the more polar fractions of the EtOAc extract has resulted in the isolation of three more pairs of stereoisomers. Based on the spectral data obtained, their structures were determined to be 3α,15α,22α-trihydroxylanosta-7,9(11),24-trien-26-oic acid [**1**], 3β,15α,22β-trihydroxylanosta-7,9(11),24-trien-26-oic acid [**2**], 3α,15α-diacetoxy-22α-hydroxylanosta-7,9(11),24-trien-26-oic acid [**3**], 3β,15α-diacetoxy-22α-hydroxylanosta-7,9(11),24-trien-26-oic acid [**4**], 22β-acetoxy-3α,15α-dihydroxylanosta-7,9(11),24-trien-26-oic acid [**5**], and 22β-acetoxy-3β,15α-dihydroxylanosta-7,9(11),24-trien-26-oic acid [**6**]. From the least polar fraction of the EtOAc extract, an additional new triterpene was also isolated and determined to be 3β,15α-diacetoxylanosta-8,24-dien-26-oic acid [**11**].

RESULTS AND DISCUSSION

Compounds **1–6** showed identical uv absorption bands at 252, 243, and 235 nm indicating that these compounds possessed heteroannular conjugated diene in the skeleton. The mass spectra of compounds **1** and **2** exhibited identical molecular ion peaks at *m/z* 486 ($C_{30}H_{46}O_5$). According to the mass fragmentation pattern assigned in the Experimental section of this report, two common fragment ion peaks at *m/z* 468 and 435 suggested that both compounds had at least two hydroxy groups. A fragment ion peak at *m/z* 417 observed in **1** and two more fragment ion peaks at *m/z* 402 and 387 observed in **2** further revealed that both **1** and **2** possessed three hydroxy groups. A common fragment ion peak at *m/z* 311 indicated that both compounds had identical side chains ($C_8H_{13}O_3$) at C-17. The upfield shift of H-3, H-15, and H-22 signals in the ^{1}H-nmr spectra of **1** and **2** as compared to those of **7** and **8** (4,22) clearly revealed the carbon positions to which the hydroxy groups were attached. A characteristic singlet at δ 3.34 in **1** and a corresponding doublet of doublets at δ 3.20 in **2** denoted β and α configuration of H-3 in **1** and **2**. The upfield shift of C-3, C-15, and C-22 and downfield shift of their adjacent carbons such as C-2, C-4, C-16, and C-23 in the ^{13}C-nmr spectra of **1** and **2**, when compared to those of **7** and **8**, suggested that both compounds were possibly the related triols of **7** and **8**. However, acetylation of **1** in Ac_2O/pyridine did not give the corresponding compound **7**, indicating that compound **1** possessed different



	R_1	R_2	R_3
1	α-OH, β-H	OH	α-OH, β-H
2	β-H, α-OH	OH	β-H, α-OH
3	α-OAc, β-H	OAc	α-OH, β-H
4	β-H, α-OAc	OAc	α-OH, β-H
5	α-OH, β-H	OH	β-H, α-OAc
6	β-H, α-OH	OH	β-H, α-OAc
7	α-OAc, β-H	OAc	β-H, α-OAc
8	β-H, α-OAc	OAc	β-H, α-OAc
9	α-OAc, β-H	OAc	H_2
10	β-H, α-OAc	OAc	H_2



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stereochemistry from **7** at C-22. Because the β configuration at C-22 of **7** was previously established by X-ray analysis (4), compound **1** was thus assigned as 3α,15α,22α-trihydroxylanosta-7,9(11),24-trien-26-oic acid. Acetylation of **2** under the same conditions gave the corresponding compound **8**, confirming that compound **2** had the structure 3β,15α,22β-trihydroxylanosta-7,9(11),24-trien-26-oic acid.

The mass spectra of compounds **3** and **4** revealed identical molecular ion peaks at *m/z* 570 ($C_{34}H_{50}O_7$) and four common fragment ion peaks at *m/z* 552, 510, 450, and 417 showing that both compounds had one hydroxy and two acetoxy groups. The presence of two common fragment ion peaks at *m/z* 353 and 293 further suggested that these two compounds had identical side chains ($C_8H_{13}O_3$) at C-17. A prominent ion

peak at *m/z* 299 observed in both compounds, due to a facile D-ring cleavage, illustrated that one of the acetoxy groups was on the D ring. A singlet at δ 4.65 in **3** and a doublet of doublets at δ 4.49 in **4** indicated that **3** had α-acetoxy and **4** had β-acetoxy at C-3 (21,22). The second acetoxy group affixed at C-15α in both **3** (δ 5.05, dd) and **4** (δ 5.04, dd) was evident when their ^{1}H-nmr spectra were compared with those of compounds **9** and **10** (21). Similar chemical shifts and coupling patterns of H-7, H-11, H-15, and H-22 (Table 1) in the ^{1}H-nmr spectra of **3** and **4** suggested that these two com-

TABLE 1. Partial ^{1}H-nmr Spectral Data of Compounds **1–6** (in $CDCl_3$, *J* = Hz).

Proton	Compound					
	1[a]	**2**[a]	**3**	**4**	**5**	**6**[a]
H-3	3.34 (1H, s)	3.20 (1H, dd, *J* = 4.5, 11.2)	4.65 (1H, s)	4.49 (1H, dd, *J* = 4.5, 11.3)	3.43 (1H, s)	3.16 (1H, dd, *J* = 4.8, 10.9)
H-7	5.78 (1H, m)	5.81 (1H, d, *J* = 5.9)	5.46 (1H, m)	5.44 (1H, d, *J* = 5.3)	5.86 (1H, m)	5.81 (1H, d, *J* = 6.5)
H-11	5.26 (1H, d, *J* = 5.2)	5.27 (1H, d, *J* = 5.7)	5.30 (1H, d, *J* = 5.6)	5.29 (1H, d, *J* = 5.3)	5.30 (1H, d, *J* = 6.1)	5.22 (1H, d, *J* = 5.5)
H-15	4.17 (1H, dd, *J* = 5.9, 9.5)	4.23 (1H, dd, *J* = 5.7, 9.5)	5.05 (1H, dd, *J* = 4.9, 9.7)	5.04 (1H, dd, *J* = 5.0, 9.8)	4.24 (1H, dd, *J* = 4.8, 9.5)	4.16 (1H, dd, *J* = 5.3, 9.6)
H-18	0.52 (3H, s)	0.57 (3H, s)	0.62 (3H, s)	0.61 (3H, s)	0.59 (3H, s)	0.53 (3H, s)
H-19	0.93 (3H, s)[b]	0.96 (3H, s)[b]	1.04 (3H, s)[b]	0.98 (3H, s)[b]	0.97 (3H, s)[b]	0.92 (3H, s)[b]
H-21	0.88 (3H, d, *J* = 7.0)	0.86 (3H, d, *J* = 6.7)	0.95 (3H, d, *J* = 7.3)	0.94 (3H, d, *J* = 6.5)	0.94 (3H, d, *J* = 6.9)	0.89 (3H, d, *J* = 6.7)
H-22	4.47 (1H, m)	3.72 (1H, m)	4.57 (1H, dd, *J* = 8.4, 14.1)	4.56 (1H, dd, *J* = 8.4, 14.3)	5.02 (1H, t, *J* = 6.7)	4.96 (1H, t, *J* = 7.0)
H-24	6.55 (1H, d, *J* = 8.9)	6.80 (1H, t, *J* = 7.1)	6.67 (1H, d, *J* = 9.1)	6.67 (1H, d, *J* = 8.8)	6.77 (1H, t, *J* = 6.8)	6.63 (1H, t, *J* = 6.8)
H-27	1.82 (3H, s)	1.81 (3H, s)	1.88 (3H, d, *J* = 0.8)	1.88 (3H, s)	1.85 (3H, s)	1.78 (3H, s)
H-28	0.88 (3H, s)[b]	0.92 (3H, s)[b]	0.96 (3H, s)[b]	0.92 (3H, s)[b]	0.94 (3H, s)[b]	0.84 (3H, s)[b]
H-29	0.87 (3H, s)[b]	0.84 (3H, s)[b]	0.86 (3H, s)[b]	0.87 (3H, s)[b]	0.91 (3H, s)[b]	0.80 (3H, s)[b]
H-30	0.93 (3H, s)[b]	0.94 (3H, s)[b]	0.97 (3H, s)[b]	0.96 (3H, s)[b]	0.95 (3H, s)[b]	0.91 (3H, s)[b]
*Me*CO	—	—	2.07 (3H, s)	2.07 (3H, s)	2.04 (3H, s)	1.99 (3H, s)
*Me*CO	—	—	2.03 (3H, s)	2.04 (3H, s)	—	—

[a]Samples were dissolved in $CDCl_3$-CD_3OD (ca. 5:1).
[b]Tentative assignments.

pounds were a pair of stereoisomers. The ^{13}C-nmr assignments of **3** and **4** (Table 2) were consistent with the proton assignments made for these two compounds. Saponification of **3** in methanolic KOH gave compound **1**, but acetylation of **3** did not give **7**, indicating that **3** and **1** had α configuration at C-22. Compound **3** was, therefore, assigned the structure 3α,15α-diacetoxy-22α-hydroxylanosta-7,9(11),24-trien-26-oic acid. Saponification of **4** did not give the same triol as **2** and acetylation of **4** afforded different triacetate from **8**, indicating that the stereochemistry of H-22 in **2** and **4** was not identical. Similar ^{13}C chemical shifts of carbons adjacent to C-22 in **1**, **3**, and **4**, which were distinct from those of compound **2**, also suggested that compounds **1**, **3**, and **4** had the same configuration at C-22. The structure of **4** was thus assigned as 3β,15α-diacetoxy-22α-hydroxylanosta-7,9(11),24-trien-26-oic acid.

The mass spectra of compounds **5** and **6** exhibited identical molecular ion peaks at *m/z* 528 ($C_{32}H_{48}O_6$), which was 42 mass units less than **3** and **4**, indicating that both compounds possessed only one acetoxy group. Three common fragment ion peaks at *m/z* 510, 468, and 417 clearly showed the presence of two hydroxy and one acetoxy group in their structures. A common fragment ion peak at *m/z* 311 further revealed that both **5** and **6** had identical side chains ($C_{10}H_{15}O_4$) at C-17, which bore an acetoxy group. Investigation of the ^{1}H-nmr spectra of **5** and **6** found that the acetoxy group was at C-22

TABLE 2. ^{13}C-nmr Spectral Data of Compounds **1–6** (in $CDCl_3$).

Carbon	Compound					
	1[a]	**2**[a]	**3**	**4**	**5**	**6**[a]
1	29.77 t	35.63 t	30.58 t	35.38 t	29.92 t	35.62 t
2	25.35 t	27.36 t	23.11 t	24.20 t	25.55 t	27.31 t
3	75.82 d	78.61 d	78.03 d	80.71 d	76.07 d	78.58 d
4	37.17 s	38.51 s	36.50 s	37.57 s	37.35 s	38.50 s
5	42.89 d	48.95 d	43.89 d	48.95 d	43.03 d	48.91 d
6	22.79 t	22.83 t	22.80 t	22.86 t	22.94 t	22.81 t
7	121.22 d	121.21 d	121.21 d	121.15 d	121.71 d	121.62 d
8	140.62 s	140.68 s	140.09 s	140.15 s	140.51 s	140.40 s
9	146.10 s	146.02 s	145.89 s	145.67 s	146.31 s	146.17 s
10	37.17 s	37.28 s	37.30 s	37.30 s	37.35 s	37.27 s
11	115.40 d	115.82 d	115.52 d	116.06 d	115.25 d	115.39 d
12	38.30 t	38.40 t	37.94 t	37.99 t	38.47 t	38.32 t
13	44.16 s	44.09 s	44.10 s	44.06 s	44.22 s	44.00 s
14	51.92 s	51.90 s	51.41 s	51.35 s	52.08 s	51.83 s
15	74.23 d	74.25 d	77.32 d	77.08 d	74.58 d	73.99 d
16	39.77 t	38.65 t	37.21 t	37.21 t	39.75 t	39.12 t
17	49.18 d	45.00 d	49.39 d	49.39 d	45.41 d	45.29 d
18	15.67 q	15.70 q	15.85 q	15.87 q	15.78 q	15.59 q
19	22.55 q	22.70 q	22.64 q	22.86 q	22.68 q	22.67 q
20	33.26 d	40.73 d	33.62 d	33.62 d	39.28 d	39.12 d
21	19.27 q	12.41 q	19.33 q	19.34 q	12.78 q	12.54 q
22	66.47 d	72.06 d	67.17 d	67.20 d	74.58 d	74.87 d
23	43.39 t	34.76 t	43.33 t	43.36 t	31.74 t	31.53 t
24	143.62 d	139.91 d	144.66 d	144.67 d	139.20 d	137.23 d
25	128.55 s	128.95 s	128.07 s	128.06 s	129.10 s	129.85 s
26	170.29 s	170.42 s	171.18 s	171.22 s	170.99 s	169.90 s
27	12.69 q	11.42 q	12.78 q	12.81 q	12.34 q	12.31 q
28	17.04 q	17.11 q	18.43 q	18.35 q	17.33 q	17.07 q
29	28.00 q	27.95 q	27.77 q	28.11 q	28.14 q	27.91 q
30	22.66 q	15.70 q	22.44 q	16.94 q	22.77 q	15.59 q
MeCO	—	—	170.81 s	170.47 s	170.62 s	171.10 s
MeCO	—	—	170.64 s	171.00 s	—	—
*Me*CO	—	—	21.41 q	21.32 q	21.03 q	20.87 q
*Me*CO	—	—	21.29 q	21.43 q	—	—

[a]Samples were dissolved in $CDCl_3$-CD_3OD (ca. 5:1).

(δ 5.02 in **5** and δ 4.96 in **6**). The two hydroxy groups were attached at C-15α (δ 4.24 in **5** and δ 4.16 in **6**) and C-3α for **5** (δ 3.43, s), C-3β for **6** (δ 3.16, dd). The ^{13}C-nmr data of **5** and **6** (Table 2) showed similar chemical shifts for most of the carbons except for those adjacent to C-3, suggesting that these two compounds were a pair of stereoisomers at C-3. Acetylation of **5** gave the corresponding triacetate **7** (4,22). The structure of compound **5** was, therefore, determined to be 22β-acetoxy-3α,15α-dihydroxylanosta-7,9(11),24-trien-26-oic acid. Saponification of **6** gave the corresponding triol **2**, and acetylation of **6** yielded the corresponding triacetate **8**, confirming that **6** and **8** had identical stereochemistry at C-22. Compound **6**, therefore, had the structure 22β-acetoxy-3β,15α-dihydroxylanosta-7,9(11),24-trien-26-oic acid. The absolute configuration of C-22 in compounds **1–6** was not determined.

The uv spectrum of compound **11** showed only end absorption band at 207 nm, indicating that this compound lacked heteroannular conjugated diene in its skeleton. Investigation of the ^{1}H-nmr spectrum of **11** confirmed the absence of H-7 and H-11 signals as observed in **1–6**. However, a triplet at δ 6.83 (J = 7.3 Hz) attributed to H-24

revealed that compound **11** had side chains identical to those of compounds **9** and **10** (21). The presence of two acetoxy groups at the C-3β and C-15α positions was based on the observations that two proton signals appeared at δ 4.47 (dd, H-3α) and 5.01 (dd, H-15β) and two acetoxy signals at δ 2.02 and 2.03. Confirmation of its structural assignment was facilitated by the analysis of its mass and ^{13}C-nmr data. Compound **11** had a molecular ion peak at *m/z* 556 ($C_{34}H_{52}O_6$), indicating that this compound possessed one less double bond than **9** and **10**. Two major fragment ion peaks at *m/z* 496 and 436 showed subsequent loss of two acetoxy groups from the molecule. Furthermore, the presence of four fragment ion peaks at *m/z* 355, 301, 295, and 241 in the mass spectrum of **11** demonstrated that its side chain ($C_8H_{13}O_2$) at C-17 and its D ring were identical to those of **9** and **10** (21). Piecing the above information together led to the deposition of the remaining double bond at C-8 (δ 132.93) and C-9 (δ 135.35). The DEPT experiments of **11** clearly showed the disappearance of these two quaternary olefinic carbons. Comparable ^{13}C chemical shifts for C-8 and C-9 were also found in closely related compounds (16,17). The structure of **11** was, therefore, established as 3β,15α-diacetoxylanosta-8,24-dien-26-oic acid.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were recorded on a Jasco UVIDEC-650 spectrophotometer. ^{1}H- and ^{13}C-nmr spectra were obtained on a Bruker AM-400 nmr spectrometer and were reported as ppm downfield from TMS (δ = 0). Mass spectra were recorded through the direct inlet of a JEOL JMS D-100 mass spectrometer at 12 and 70 eV and were recorded as *m/z*. Melting points were determined on a Fisher-Johns melting point apparatus and were uncorrected.

CULTURE OF *G. LUCIDUM*.—*G. lucidum* of the strain TP-1 was collected locally and deposited at the Institute of Botany, Academia Sinica, Republic of China. This strain was maintained on potato-dextrose-agar slants. The culture conditions for mycelial growth have been described previously (21).

ISOLATION AND PURIFICATION.—Mycelia were harvested from a 30-day-old liquid culture (300 ml × 30, in 1-liter culture flasks) of *G. lucidum*. After filtration through four layers of cheesecloth and a gentle rinse with H_2O, the dried biomass (56 g) was ground into powder and extracted with MeOH. The concentrated extracts were partitioned between *n*-hexane and H_2O. The aqueous layer was re-extracted with EtOAc. The pooled EtOAc fraction was chromatographed on a Si gel column (45 × 2.5 cm) by stepwise elution with increasing percentages of MeOH in $CHCl_3$. Fractions containing **3–6** were combined and chromatographed on tlc [E. Merck, Kieselgel 60 F_{254}; 0.25 mm thickness; *n*-hexane-Et_2O-EtOAc-HOAc (1:1:1:0.005)]. Eluting the band at R_f 0.27 with 5% MeOH in $CHCl_3$ gave a mixture of **3** and **4**, and eluting the band at R_f 0.24 afforded a mixture of **5** and **6**. The mixture of **3** and **4** was further purified by hplc using a semipreparative reversed-phase column (LiChrosorb C_{18}, 250 × 7 mm). Compounds **3** (1.1 mg) and **4** (3.2 mg) were well separated by eluting with 80% aqueous MeOH. Complete separation of **5** (2.6 mg) and **6** (3.4 mg) was also achieved by hplc using the same conditions (24).

Purification of the more polar fractions by tlc (*n*-hexane-Et_2O-EtOAc-HOAc, 1:1:1:0.005, triple development) gave three bands. The band at R_f 0.08 was further separated into two bands when $CHCl_3$-Et_2O-MeOH (9:1:1, triple development) was used as developing solvent. Eluting the band at R_f 0.15 with 5% MeOH in $CHCl_3$ afforded **1** (3.1 mg), and eluting the band at R_f 0.22 yielded **2** (1.8 mg). Purification of the least polar fractions of EtOAc extract by reversed-phase hplc using MeCN-HOAc (100:0.5) as eluent gave **11** (6.2 mg).

CHARACTERIZATION OF COMPOUND **1**.—Uv λ max (MeOH) (log ε) 225 (4.08), 235 (4.11), 243 (4.13), 252 nm (3.96); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 486 ($C_{30}H_{46}O_5$) (100), $[M-H_2O]^+$ 468 (44), $[M-2H_2O-Me]^+$ 435 (9), $[M-3H_2O-Me]^+$ 417 (9), $[M-C_8H_{13}O_3$ side chain $-H_2O]^+$ 311 (13).

CHARACTERIZATION OF COMPOUND **2**.—Colorless needles, mp 178–180° ($CHCl_3$/MeOH); uv λ max (MeOH) (log ε) 226 (4.19), 235 (4.19), 243 (4.19), 252 nm (4.00); ^{1}H nmr see table 1; ^{13}C nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 486 ($C_{30}H_{46}O_5$) (100), $[M-H_2O]^+$ 468 (10), $[M-H_2O-Me]^+$ 453 (14), $[M-2H_2O-Me]^+$ 435 (7), $[M-3H_2O-2Me]^+$ 402 (7), $[M-3H_2O-3Me]^+$ 387 (7), $[M-C_8H_{13}O_3$ side chain $-H_2O]^+$ 311 (17).

CHARACTERIZATION OF COMPOUND **3**.—Uv λ max (MeOH) (log ε) 216 (4.15), 227 (4.12), 235 (4.12), 243 (4.13), 252 nm (3.95); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 570

($C_{34}H_{50}O_7$) (97), $[M-H_2O]^+$ 552 (35), $[M-HOAc]^+$ 510 (19), $[M-HOAc-Me]^+$ 495 (28), $[M-HOAc-H_2O-Me]^+$ 477 (14), $[M-2HOAc]^+$ 450 (19), $[M-2HOAc-Me]^+$ 435 (42), $[M-2HOAc-H_2O-Me]^+$ 417 (75), [M − $C_8H_{13}O_3$ side chain − HOAc]$^+$ 353 (52), [D-ring cleavage − Me]$^+$ 299 (30), [M − $C_8H_{13}O_3$ side chain − 2HOAc]$^+$ 293 (69), [299 − HOAc]$^+$ 239 (100).

CHARACTERIZATION OF COMPOUND **4**.—Uv λ max (MeOH) (log ε) 216 (4.14), 227 (4.11), 235 (4.11), 243 (4.12), 252 nm (3.95); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; ms *m/z* (rel. int.) [M]$^+$ 570 ($C_{34}H_{50}O_7$) (100), $[M-H_2O]^+$ 552 (18), $[M-HOAc]^+$ 510 (11), $[M-HOAc-Me]^+$ 495 (14), $[M-HOAc-H_2O-Me]^+$ 477 (4), $[M-2HOAc]^+$ 450 (7), $[M-2HOAc-Me]^+$ 435 (14), $[M-2HOAc-H_2O-Me]^+$ 417 (21), [M − $C_8H_{13}O_3$ side chain − HOAc]$^+$ 353 (10), [D-ring cleavage − Me]$^+$ 299 (16), [M − $C_8H_{13}O_3$ side chain − HOAc]$^+$ 293 (11), [299 − HOAc]$^+$ 239 (18).

CHARACTERIZATION OF COMPOUND **5**.—Uv λ max (MeOH((log ε) 217 (4.12), 235 (4.09), 243 (4.09), 252 nm (3.92); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; ms *m/z* (rel. int.) [M]$^+$ 528 ($C_{32}H_{48}O_6$) (100), $[M-H_2O]^+$ 510 (9), $[M-H_2O-Me]^+$ 495 (10), $[M-HOAc]^+$ 468 (11), $[M-HOAc-H_2O]^+$ 450 (7), $[M-HOAc-2H_2O-Me]^+$ 417 (9), [M − $C_{10}H_{15}O_4$ side chain − H_2O]$^+$ 417 (8).

CHARACTERIZATION OF COMPOUND **6**.—Uv λ max (MeOH) (log ε) 217 (4.13), 235 (4.09), 243 (4.10), 252 nm (3.95); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; ms *m/z* (rel. int.) [M]$^+$ 528 ($C_{32}H_{48}O_6$) (100), $[M-H_2O]^+$ 510 (12), $[M-H_2O-Me]^+$ 495 (18), $[M-HOAc]^+$ 468 (35), $[M-HOAc-H_2O]^+$ 450 (12), $[M-HOAc-2H_2O-Me]^+$ 417 (24), [M − $C_{10}H_{15}O_4$ side chain − H_2O]$^+$ 311 (32).

CHARACTERIZATION OF COMPOUND **11**.—Uv λ max (MeOH) (log ε) 207 nm (4.30); ^{1}H nmr δ ($CDCl_3$) 6.83 (1H, t, J = 7.3 Hz, H-24), 5.01 (1H, dd, J = 4.8, 9.4 Hz, H-15), 4.47 (1H, dd, J = 4.3, 11.5 Hz, H-3), 2.03 (3H, s, *Me*CO), 2.02 (3H, s, *Me*CO), 1.80 (3H, s, H-27), 0.97 (6H, s, H-19, H-30), 0.89 (3H, d, J = 6.3 Hz, H-21), 0.85 (6H, s, H-28,m H-29), 0.75 (3H, s, H-18); ^{13}C nmr δ ($CDCl_3$) 172.56 (s, C-26), 171.11 (s, MeCO), 171.06 (s, MeCO), 145.23 (d, C-24), 135.35 (s, C-9), 132.93 (s, C-8), 126.68 (s, C-25), 80.80 (d, C-3), 76.01 (d, C-15), 50.98 (s, C-14), 50.28 (d, C-5), 49.03 (d, C-17), 44.68 (s, C-13), 37.76 (s, C-4), 36.96 (s, C-10), 36.50 (t, C-16), 36.19 (d, C-20), 35.16 (t, C-1), 34.63 (t, C-22), 31.08 (t, C-12), 27.92 (q, C-29), 26.30 (t, C-6), 25.90 (t, C-23), 24.09 (t, C-2), 21.40 (q, *Me*CO), 21.31 (q, *Me*CO), 20.76 (t, C-11), 19.11 (q, C-19), 18.24 (q, C-28), 18.18 (q, C-21), 18.04 (t, C-7), 16.52 (q, C-30), 16.09 (q, C-18), 11.99 (q, C-27); ms *m/z* (rel. int.) [M]$^+$ 556 ($C_{34}H_{52}O_6$) (11), $[M-HOAc]^+$ 496 (80), $[M-HOAc-Me]^+$ 481 (23), $[M-2HOAc]^+$ 436 (100), $[M-2HOAc-Me]^+$ 421 (47), [M − $C_8H_{13}O_2$ side chain − HOAc]$^+$ 355 (25), [D-ring cleavage − Me]$^+$ 301 (44), [M − $C_8H_{13}O_2$ side chain − 2HOAc]$^+$ 295 (20), [D-ring cleavage − HOAc]$^+$ 241 (43).

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