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Novel Triterpenoids from the Aerial Roots of *Ficus microcarpa*

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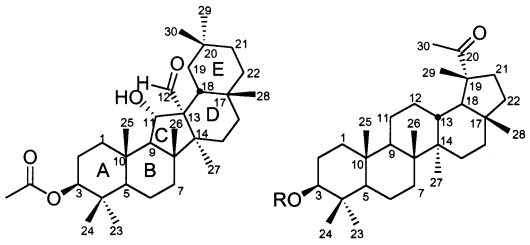
Three novel triterpenoids, 3β-acetoxy-11α-hydroxy-11(12→13)abeooleanan-12-al (**1**), 3β-hydroxy-20-oxo-29(20→19)abeolupane (**2**), and 29,30-dinor-3β-acetoxy-18,19-dioxo-18,19-secolupane (**3**), and the known **4**, **5a**, and **5b** were isolated from the aerial roots of *Ficus microcarpa*. Their structures were elucidated on the basis of 2D NMR and X-ray diffraction experiments. Compound **1**, derived from the oleanane skeleton, has an unusual five-membered C ring. Compounds **2** and **3**, derived from the lupane skeleton, have unique skeletons that may arise from the same biogenetic pathway.

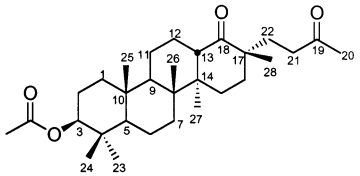
Introduction

Ficus microcarpa L. f. (Moraceae) is a popular ornamental plant in Taiwan. Phytochemical studies of this plant have led to the identification of triterpenoids from the leaves,[1] fruits,[2] bark,[3] and aerial roots.[4] In the present study, three novel triterpenoids **1**−**3**, which have unique skeletons, were isolated from the aerial roots. The structural elucidation and proposed biogenetic pathways of these compounds are reported here.



1

2 R = H
2a R = (*S*)-MTPA
2b R = (*R*)-MTPA



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Results and Discussion

Compound **1** was isolated as a colorless solid. The molecular formula $C_{32}H_{52}O_4$ was established by its ^{13}C NMR and HREIMS data, representing seven indices of hydrogen deficiency (IHD). The IR spectrum of **1** showed absorptions for hydroxyl (3520 cm^{-1}) and acetoxyl (1734, 1248 cm^{-1}) functionalities. The ^1H NMR (Table 1) spectrum in $CDCl_3$ exhibited signals for eight singlet methyl groups [δ_H 0.74, 0.83, 0.85, 0.91, 0.95, 1.02, 1.04, 1.06], one acetoxyl group [δ_H 2.02 (s)], one methine proton attached with the acetoxyl group [δ_H 4.49 (dd, J = 8.4, 8.0 Hz, H-3)], one carbinyl proton [δ_H 3.81 (td, J = 12.0, 1.6 Hz, H-11)], an exchangeable hydroxyl proton [δ_H 4.00 (d, J = 12.0 Hz)], and one aldehyde [δ_H 9.81 (d, J = 1.6 Hz, H-12)]. ^{13}C NMR (Table 1) and DEPT spectra of **1** indicated nine CH_3, nine CH_2, six CH, and eight C, including one acetoxy (δ_C 21.3, 170.9), one aldehyde (δ_C 209.3), and two carbons to which oxygen was attached (δ_C 80.7, 82.2). Because the IHD of **1** was seven including one acetoxy and one aldehyde functionality, the number of rings in **1** should be five. The structure of **1** was proposed as an oleanane derivative on the basis of ^{13}C NMR data similar to that of the oleanane derivatives isolated from the same source.[4b] Besides eight singlet methyl groups, an additional aldehyde gave a suggestion that one of the six-membered rings was constricted to form a five-membered ring and an aldehyde. Comparison of the ^{13}C NMR data between **1** and **4**[4b] revealed that the obvious difference was in ring C. 12-Oleanene derivatives with C-11α OH, OMe, or OEt will have H-1β shifted downfield to about δ_H 2.[4b] Compound **1** showed H-1β at δ_H 2.28 (dt, J = 14.0, 3.6 Hz), suggesting the C-11α position for the hydroxyl group. An HMBC experiment confirmed the assigned structure (Table 1). NOESY correlations of the aldehydic proton (H-12) with H-19α, H_3-27, and H_3-29 indicated that the aldehyde was α-oriented. The hydroxyl proton absorbed at δ_H 4.00 (d, J = 12.0 Hz), indicating a hydrogen bond to the aldehyde and proving the relative stereochemistry of H-11α and CHO-12 (Figure 1). This rigid conformation gave the ∠HOCH close to 180°, consistent with the 12.0 Hz coupling constant, and causing the W form coupling between H-11

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TABLE 1. NMR Data for Compound 1 (100 and 400 MHz in $CDCl_3$, *J* in Hz)

position	δ_C, mult	δ_H	HMBC	COSY	NOESY
1	39.1 t	2.28 dt (14.0, 3.6, H_β), 1.25[a] (H_α)	H_3-25	H1α, H_2-2	H1α, H_2-2, OH
				H1α, H_2-2	H1β, H3, OH
2	23.4 t	1.63[a]		H3	H1β, H3
3	80.7 d	4.49 dd (8.4, 8.0)	H_3-23, H_3-24	H_2-2	H1α, H_2-2, H5, H_3-23
4	37.4 s		H_3-23, H_3-24		
5	56.2 d	0.83[a]	H_3-23, H_3-24, H_3-25		H3
6	18.5 t	1.55[a], 1.40[a]			
7	35.9 t	1.30−1.50[a]	H_3-26		
8	44.4 s		H9, H_3-26, H_3-27		
9	58.6 d	1.48 d (12.0)	H11, H_3-25, H_3-26	H11	OH
10	37.9 s		H_3-25		
11	82.2 d	3.81 td (12.0, 1.6)	H9, H12	H9, H12, OH	H18, H19β, H_3-25, H_3-26
12	209.3 d	9.81 d (1.6)	H11, H18	H11	H19α, H_3-27, H_3-29
13	62.2 s		H11, H12, H18, H_3-27		
14	51.2 s		H_3-26, H_3-27		
15	26.0 t	1.98[a], 0.95[a]	H_3-27	H_2-16	H_2-16
16	34.4 t	1.60[a], 1.20[a]	H18, H_3-28	H_2-15	H_2-15
17	32.9 s		H_3-28		
18	47.1 d	1.64[a]	H_2-19, H_3-28	H_2-19	H11, H19β
19	33.7 t	1.93[a] (H_β), 1.40[a] (H_α)	H_3-29, H_3-30	H18, H19α	H11, H18, H_3-30
				H18, H19β	H12
20	29.0 s		H_3-29, H_3-30		
21	35.4 t	1.30−1.50[a]	H_3-29, H_3-30		
22	36.4 t	1.30−1.50[a]	H_3-28		
23	28.2 q	0.83 s	H3, H_3-24		H3
24	16.5 q	0.85 s	H3, H_3-23		H_3-25
25	16.8 q	1.02 s			H11, H_3-24
26	20.7 q	1.04 s			H11
27	23.4 q	0.95 s			H12
28	27.9 q	1.06 s			
29	28.3 q	0.74 s	H_3-30		H12
30	34.8 q	0.91 s	H_3-29		H19β
CH_3CO	170.9 s		CH_3CO		
CH_3CO	21.3 q	2.02 s			
OH		4.00 d (12.0)			H_2-1, H9

[a] Data obtained from HMQC spectrum.

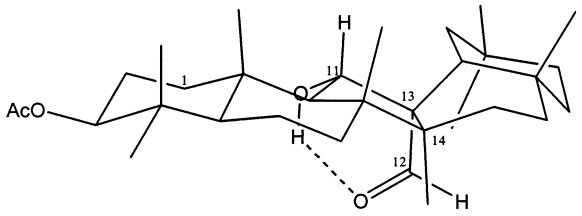
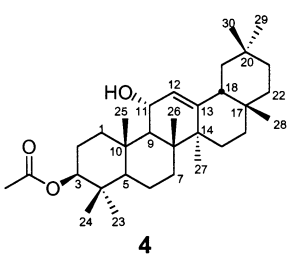


FIGURE 1. Hydrogen bonding conformation of **1**.

and H-12 (−C*H*O) of 1.6 Hz. After the addition of D_2O in $CDCl_3$ solution, the signal at δ_H 4.00 disappeared and the signal of H-11 (δ_H 3.81) become a double doublet (J = 12.0, 1.6 Hz). Therefore, compound **1** was unambiguously assigned as 3β-acetoxy-11α-hydroxy-11(12→13)-abeooleanan-12-al. The biosynthesis of this new skeleton may occur from compound **4**, which is oxidized with monooxygenase to give **6**. Opening the epoxide with ring contraction gives compound **1** (Scheme 1).



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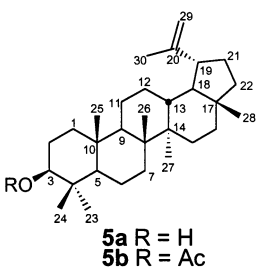

5a R = H
5b R = Ac

Compound **2**, a colorless solid, analyzed for $C_{30}H_{50}O_2$, which required IHD six on the basis of its combined HREIMS and ^{13}C NMR spectra. Its IR spectrum showed hydroxyl (3442 cm^{-1}) and ketone (1705 cm^{-1}) functionalities. The ^1H NMR spectrum (Table 2) of **2** exhibited signals for seven singlet methyl groups [δ_H 0.74, 0.80, 0.94, 0.94, 0.97, 1.01, 1.20], one acetyl group [δ_H 2.12], a methine proton [δ_H 1.95 (d, J = 12.0 Hz, H-18)], and one carbinyl proton [δ_H 3.16 (dd, J = 11.2, 4.8 Hz, H-3)]. The ^{13}C NMR spectrum exhibited 30 signals (eight CH_3, ten CH_2, five CH, and seven C) including one acetyl ketone (δ_C 213.9, C-20) and one oxygenated carbon (δ_C 78.9, C-3). Lupenol (**5a**),[5] isolated from the same source, has similar ^1H and ^{13}C NMR data (Table 2) for the A, B, and C rings. Thus, structure **2** may be derived from a lupane-type triterpene. In the HMBC spectrum (Table 2), the long-range $^{13}C-^1H$ correlations C-18/H_3-29; C-19/H-18, H-21β, H_3-29; C-20/H-18, H_3-29, H_3-30; and C-21/H_3-29 established the partial structure on the E ring (Figure 2a). NOESY correlations for H_3-27/H-18; H_3-28/H_3-29; and H_3-30/H-18, H-21α, H_3-29 suggested that CH_3-29 should be on the same face as H-13 and CH_3-28 (Figure 2b). This novel structure was confirmed by a single-crystal X-ray diffraction study (Figure 3). The absolute configuration of **2** was determined by the modified Mosher's method.[6]

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SCHEME 1. Proposed Mechanism for Biosynthesis of 1 from 4

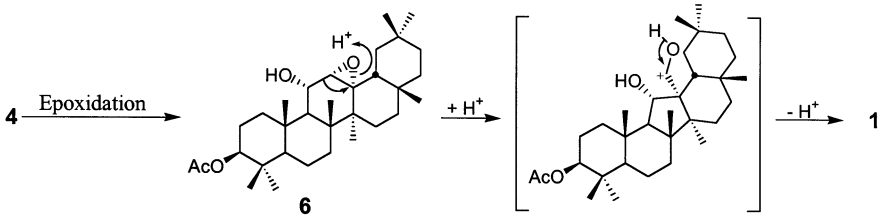


TABLE 2. NMR Data for Compound 2 (100 and 400 MHz in $CDCl_3$, *J* in Hz)

position	δ_C, mult	δ_H	HMBC	COSY	NOESY
1	38.6 t	1.63[a], 0.88[a]	H_3-25		
2	27.4 t	1.58[a]		H3	H3
3	78.9 d	3.16 dd (11.2, 4.8)	H_3-23, H_3-24	H_2-2	H_2-2, H5, H_3-23
4	38.9 s		H_3-23, H_3-24		
5	55.3 d	0.67 br d (9.6)	H_3-23, H_3-24, H_3-25	H_2-6	H3, H9
6	18.3 t	1.52[a], 1.36[a]		H5	
7	34.2 t	1.37[a]	H_3-26		
8	40.9 s		H_3-26, H_3-27		
9	50.6 d	1.30[a]	H_3-25, H_3-26		H5
10	37.2 s		H_3-25		
11	20.8 t	1.41[a]			
12	25.4 t	1.58[a], 1.21[a]			
13	34.7 d	1.71 td (12.0, 2.8)	H18, H_3-27	H18	H_3-26, H_3-29
14	43.2 s		H_3-25, H_3-26		
15	27.5 t	1.02[a]			
16	37.8 t	1.47[a], 1.43[a]			
17	43.4 s		H18, H_3-28		
18	50.8 d	1.95 d (12.0)	H_3-28, H_3-29	H13	H_3-27, H_3-30
19	54.9 s		H18, H21β, H_3-29		
20	213.9 s		H18, H_3-29, H_3-30		
21	37.8 t	1.86 ddd (12.8, 8.8, 4.0, H_α), 1.58[a] (H_β)	H_3-29	H_2-22	H_2-22, H_3-30
					H_2-22
22	40.5 t	1.56[a], 1.30[a]	H_3-28	H_2-21	H_2-21
23	28.0 q	0.94 s	H_3-24		H3
24	15.3 q	0.74 s	H_3-23		
25	16.1 q	0.80 s			H_3-26
26	16.0 q	1.01 s			H13, H_3-25
27	15.3 q	0.97 s			H18
28	20.1 q	0.94 s	H18		H_3-29
29	20.2 q	1.20 s	H18		H13, H_3-28, H_3-30
30	25.4 q	2.12 s			H18, H21α, H_3-29

[a] Data obtained from HMQC spectrum.

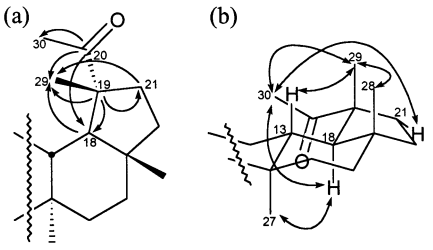


FIGURE 2. (a) Selected HMBC correlations and (b) selected NOESY correlations of **2**.

Treatment of **2** with (*R*)- and (*S*)-2-methoxy-2-trifluoromethyl-2-phenylacetyl chloride (MTPACl) afforded the (*S*)- and (*R*)-MTPA esters (**2a** and **2b**, respectively). $\Delta\delta$ values ($\delta_S - \delta_R$) of H_3-23 (+32.0) and H_3-24 (+6.4) showed positive values, while H_3-25 (−7.6) was negative (Figure 4), thus indicating a 3*S*-configuration. Therefore, Compound **2** was assigned as (3*S*)-3β-hydroxy-20-oxo-29-(20→19)abeolupane.

Triterpene **3** had HREIMS and ^{13}C NMR data consistent with the molecular formula $C_{30}H_{48}O_4$. The IR spectrum of **3** showed the presence of an acetoxyl group (1735 and 1248 cm^{-1}) and two ketone carbonyl groups (1718 and 1706 cm^{-1}) that were confirmed by ^{13}C NMR and DEPT experiments. The ^1H NMR spectrum (Table 3) of **3** exhibited signals for six singlet methyl groups [δ_H 0.75, 0.82, 0.83, 0.88, 1.10, 1.13], one acetyl group [δ_H 2.13 (s, H_3-20)], one acetoxyl group [δ_H 2.02 (3H, s)], a methylene

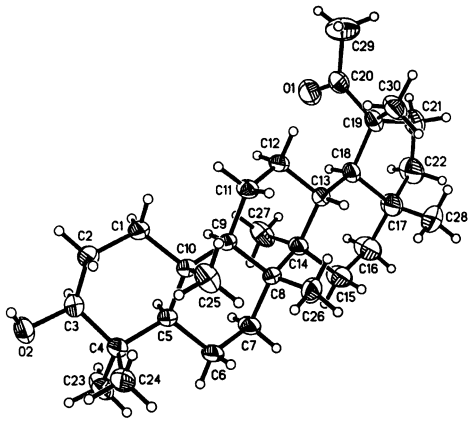


FIGURE 3. ORTEP drawing of **2**.

TABLE 3. NMR Data for Compound 3 (100 and 400 MHz in $CDCl_3$, *J* in Hz)

position	δ_C, mult	δ_H	HMBC	COSY	NOESY
1	38.6 t	1.71[a](H_β), 1.05 td (12.4, 4.8, H_α)		H1α, H_2-2	H1α
				H1*β*, H_2-2	H1*β*
2	23.6 t	1.62[a]		H_2-1, H3	H3
3	80.7 d	4.45 dd (11.2, 5.6)	H_3-23, H_3-24	H_2-2	H_2-2, H5, H_3-23
4	37.8 s		H3, H_3-23, H_3-24		
5	55.5 d	0.80[a]	H_3-23, H_3-24, H_3-25	H_2-6	H3
6	18.1 t	1.54[a], 1.30[a]		H5	
7	34.0 t	1.71[a], 1.51[a]	H_3-26		H_3-27
8	40.9 s		H_3-26, H_3-27		
9	50.8 d	1.21[a]	H_3-25, H_3-26	H_2-11	
10	37.2 s		H_3-25		
11	20.0 t	1.54[a]		H9	H_3-25
12	22.1 t	1.62[a], 1.28[a]	H13	H13	
13	47.9 d	2.67 dd (11.6, 4.0)	H_3-27	H_2-12	H15*β*, H_3-26, H_3-28
14	46.5 s		H_2-12, H_3-25, H_3-26		
15	26.8 t	2.02[a] (H_β), 1.28 (H_α)	H_3-27	H_2-16	H13, H15α, H16*β*, H_3-26, H_3-28
				H_2-16	H15*β*
16	34.0 t	1.71[a] (H_α), 1.51[a] (H_β)	H_3-28	H_2-15	H_3-27
				H_2-15	H15*β*
17	46.3 s		H13, H_2-15, H_2-16, H_2-21, H_2-22, H_3-28		
18	217.6 s		H13, H_2-22, H_3-28		
19	209.4 s		H_3-20, H_2-21, H_2-22		
20	29.9 q	2.13 s			H_2-21
21	38.9 t	2.49 dt (16.8, 6.4, H_a)	H_3-20, H_2-22	H_2-22	H_3-20, H_2-22, H_3-28
		2.42 dt (16.8, 6.4, H_b)		H_2-22	H_3-20, H_2-22, H_3-28
22	32.2 t	1.65[a]	H_2-21, H_3-28	H_2-21	H_2-21
23	27.9 q	0.83 s	H_3-24		H3
24	16.5 q	0.82 s	H_3-23		
25	16.7 q	0.88 s			H_2-11, H_3-26
26	16.0 q	1.10 s			H13, H15*β*, H_3-25
27	16.0 q	0.75 s			H_2-7, H16α
28	24.3 q	1.13 s	H_2-22		H13, H15*β*, H_2-21
CH_3CO	171.0 s		H3, CH_3CO		
CH_3CO	21.3 q	2.02 s			

[a] Data obtained from HMQC spectrum.

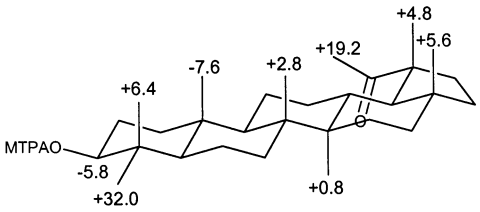


FIGURE 4. $\Delta\delta$ values [$\Delta\delta$ (in Hz) = $\delta_S - \delta_R$] obtained for the (*S*)- and (*R*)-MTPA esters (**2a** and **2b**, respectively).

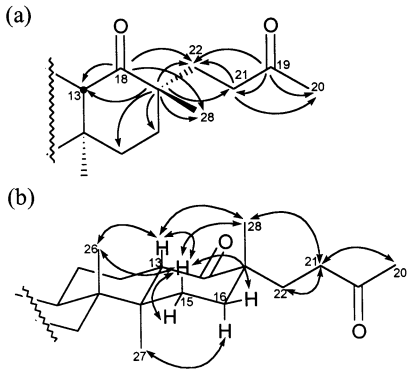
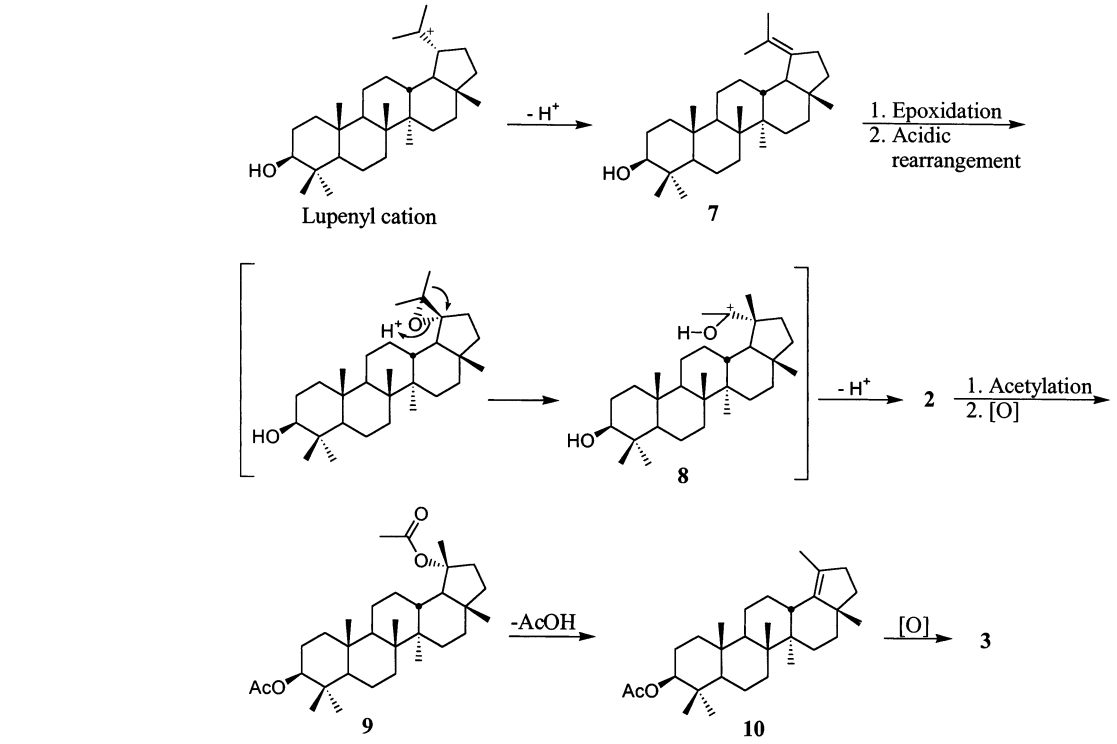


FIGURE 5. (a) Selected HMBC correlations and (b) selected NOESY correlations of **3**.

flanked by a ketone and a secondary carbon [δ_H 2.42, 2.49 (both 1H, dt, J = 16.8, 6.4 Hz, H_2-21)], a methine proton next to a ketone [δ_H 2.67 (dd, J = 11.6, 4.0 Hz, H-13)], and a methine proton attached to an acetoxyl group [δ_H 4.45 (dd, J = 11.2, 5.6 Hz, H-3)]. The ^{13}C NMR and DEPT spectra (Table 3) exhibited 30 signals (eight CH_3, ten CH_2, four CH, and eight C), with chemical shift values suggesting the presence of three carbonyl groups [δ_C 171.0, OAc; 209.4, C-19; 217.6, C-18]. The presence of these features suggested that **3** was a dinortriterpenoid that contained four carbocyclic rings. Lupenol acetate (**5b**),[5] isolated from the same source, has similar ^1H and ^{13}C NMR data for the A and B rings. HMQC and HMBC measurements (Table 3) allowed ring D and the side chain to be fully constructed (Figure 5a). In the MS, γ-H McLafferty rearrangements (Figure 6) confirmed the side chain moiety. NOESY correlations for H-13/H-15*β*, H_3-26, H_3-28; H-15*β*/H-13, H-15α, H-16*β*, H_3-26, H_3-28; H-16α/H_3-27; and H_2-21/H_3-20, H_2-22, H_3-28 suggested that CH_3-28 should be on the same face as H-13, H-15*β*, and H_3-26 (Figure 5b). Therefore, compound **3** was assigned as 29,30-dinor-3*β*-acetoxy-18,19-dioxo-18,19-secolupane, with a novel skeleton.

Compounds **2** and **3** may be derived from the lupenyl cation (Scheme 2). Deprotonation of the lupenyl cation yields **7**, which is converted to intermediate **8** by epoxidation and then acidic rearrangement. After deprotonation, compound **2** is produced. Acetylation and then Baeyer−Villiger-type oxidation of **2** yields **9**. After elimination of one molecular of acetic acid, compound **10** is produced. Further oxidation catalyzed by dioxygenase gives compound **3**.

SCHEME 2. Proposed Mechanism for Biosynthesis of 2 and 3 from Lupenyl Cation



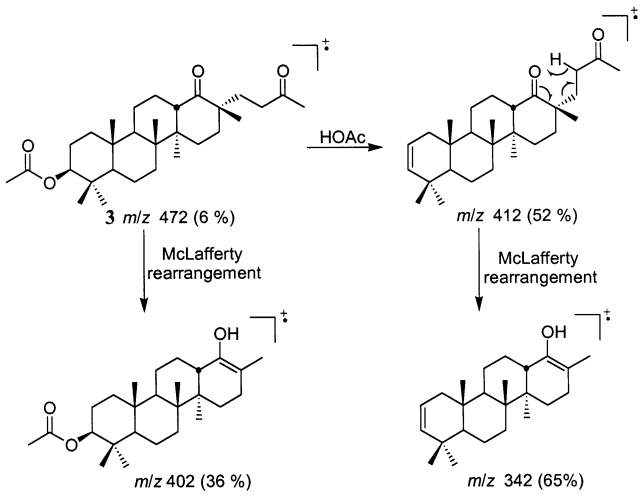


FIGURE 6. MS fragments from McLafferty rearrangement of **3**.

Experimental Section

General Methods. Melting points were determined with a micromelting point apparatus and are uncorrected. The X-ray crystallographic data were collected using graphic-monochromated Mo Kα radiation. Extracts were chromatographed over silica gel (Merck 70−230 mesh, 230−400 mesh, ASTM).

Plant Material. The aerial roots of *Ficus microcarpa* L. f. were collected on the campus of National Taiwan University, Taiwan, in 1996. The plant was identified by Mr. Muh-Tsuen Gun, formerly a technician of the Department of Botany, National Taiwan University. A voucher specimen (no. 038671) has been deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan.

Extraction and Isolation. The dried aerial roots of *Ficus microcarpa* L. f. were crushed to give 18 kg of raw material, which was extracted with MeOH (150 L) at room temperature (7 days × 2). The extract was evaporated in vacuo to yield a residue, which was suspended in H_2O (1 L) and then partitioned with ethyl acetate (1 L × 3). The combined ethyl acetate layer afforded a black syrup (250 g), which was subsequently chromatographed over silica gel with a hexane/EtOAc gradient solvent system. Crude compound **1** was eluted with 2% EtOAc in hexane. Further purification by HPLC [Merck Si 60 (7μm)] gave **1** (5 mg) using 3% EtOAc in hexane. A crude mixture of compounds **2** and **3** was eluted with 30% EtOAc in hexane. Further purification by HPLC [Merck Si 60 (7μm)] gave **2** (8 mg) and **3** (7 mg) using 3% acetone in CH_2Cl_2.

3β-Acetoxy-11α-hydroxy-11(12→13)abeooleanan-12-al (1): colorless solid, mp 215−220 °C; IR ν_{max} 3520, 1734, 1386, 1370, 1248, 1030, 985, 737 cm^{-1}; $[\alpha]^{25}_D$ +0.76° ($CHCl_3$, *c* 0.4); ^{1}H and ^{13}C NMR data, Table 1; EIMS *m*/*z* (rel intensity) 500(M^+, 1), 482(9), 466(20), 464(15), 422(24), 407(30), 271(24), 253(24), 232(25), 221(100), 203(39), 189(88), 175(50), 95(69); HREIMS *m*/*z* 500.3856 (M^+ calcd $C_{32}H_{52}O_4$, 1.2 mmu).

3β-Hydroxy-20-oxo-29(20→19)abeolupane (2): colorless solid, mp 275−277 °C; IR ν_{max} 3442, 1705, 1385, 1362, 1257, 1047, 1029, 990, 736 cm^{-1}; $[\alpha]^{21}_D$ +16.3° ($CHCl_3$, *c* 0.2); ^{1}H and ^{13}C NMR data, Table 2; EIMS *m*/*z* (rel intensity) 442(M^+, 6), 425(17), 424(49), 409(23), 381(79), 355(17), 313(20), 245(26), 203(42), 189(100), 175(52), 161(61), 121(82), 107(81), 95(73); HREIMS *m*/*z* 442.3807 (M^+ calcd for $C_{30}H_{50}O_2$, 0.6 mmu).

29,30-Dinor-3β-acetoxy-18,19-dioxo-18,19-secolupane (3): colorless solid, mp 183−186 °C; IR ν_{max} 1735, 1718, 1706, 1382, 1372, 1248, 1030, 1010, 982, 736 cm^{-1}; $[\alpha]^{21}_D$ +24.0° ($CHCl_3$, *c* 0.3); ^{1}H and ^{13}C NMR data, Table 3; EIMS *m*/*z* (rel intensity) 472(M^+, 6), 412(52), 402(36), 397(48), 369(100), 342(65), 301((30), 209(73), 191(84), 189(96), 161(52), 119(63), 109(67), 93(67); HREIMS *m*/*z* 472.3560 (M^+ calcd for $C_{30}H_{48}O_4$, 0.6 mmu).

(*S*)-MTPA Ester (2a) from 2. To a CH_2Cl_2 solution (100 μL) of compound **2** (1.2 mg) were added 4-(dimethylamino)-pyridine (25 μg), triethylamine (10 μL), and (*R*)-MTPACl (5 μL) at room temperature, and stirring was continued for 3 h. After addition of triethylamine (10 μL) and evaporation of solvent, the residue was passed through a silica gel column

(hexane/EtOAc, 20:1) to afford the (*S*)-MTPA ester (**2a**, 0.7 mg) of **2**. **2a**: colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (s, H_3-24), 0.82 (s, H_3-25), 0.86 (s, H_3-23), 0.96 (s, H_3-28), 0.98 (s, H_3-27), 1.02 (s, H_3-26), 1.21 (s, H_3-29), 2.18 (s, H_3-30), 4.68 (dd, J = 11.6, 4.4 Hz, H-3); EIMS (70 eV) *m*/*z* (rel intensity) 658 (M^+, 5), 615 (5), 425 (52), 424 (46), 381 (42), 189 (100).

(*R*)-MTPA Ester (2b) from 2. Compound **2** (1.1 mg) was treated with (*S*)-MTPACl (5 μL) by the above procedure to afford the (*R*)-MTPA ester (**2b**, 0.5 mg) of **2**. **2b**: colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (s, H_3-24), 0.78 (s, H_3-23), 0.84 (s, H_3-25), 0.95 (s, H_3-28), 0.98 (s, H_3-27), 1.01 (s, H_3-26), 1.20 (s, H_3-29), 2.13 (s, H_3-30), 4.68 (dd, J = 11.6, 4.4 Hz, H-3); EIMS (70 eV) *m*/*z* (rel intensity) 658 (M^+, 3), 615 (3), 425 (31), 424 (25), 381 (23), 189 (100).

X-ray Crystal Structure Analysis of 2. A colorless crystal of **2** with dimensions 0.35 × 0.20 × 0.20 mm^3 was selected for X-ray analysis. Structure analysis was performed using the SHELXTL program on PC.[7] Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. The compound crystallized in the monoclinic space group $P2_1$, with a = 12.662 (3) Å, b = 6.8170 (14) Å, c = 15.405 (3) Å, β = 94.87 (3)°, V = 1324.9 (5) Å^3, Z = 2, D_{calc} = 1.110 g/cm^3, λ = 0.71073 Å, μ(Mo Kα) = 0.067 mm^{-1}, F(000) = 492, and T = 295 (2) K. The SMART program was used to make data corrections. A total of 24606 reflections, collected in the range 2.17° ≤ θ ≤ 27.49°, yielded 5869 unique reflections. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 values for 5595 reflections with $I > 2\sigma(I)$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using ariding mode. The final indices were R = 0.0523, R_w = 0.1493 with goodness-of-fit = 1.123. Scattering factors were taken from the *International Tables for X-ray Crystallography*.[8]

Acknowledgment. This research was supported by the National Science Council of the Republic of China.

Supporting Information Available: ^{1}H and ^{13}C NMR, HMQC, HMBC, COSY, NOESY, IR, and MS spectral data for compounds **1**−**3** and X-ray crystal structure data of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Sheldrick, G. M. *SHELXTL/PC*, Version 5.03; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(8) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.