Novel Nortriterpenoids from *Aphanamixis grandifolia*

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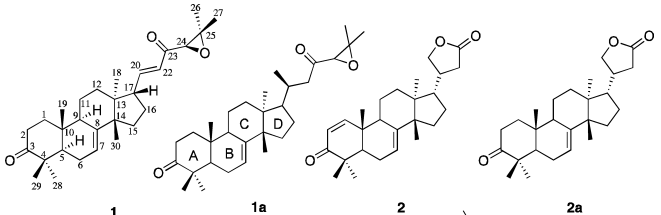
Four novel nortriterpenoids, 24,25-epoxy-tirucall-7,20(*E*)-diene-3,23-dione (1), 24,25,26,27-tetranortirucall-1,7-diene-23(21)-lactone (2), 3α-hydroxy-tirucall-7-ene-20-one (3), and 3-oxo-tirucall-7-ene-3,20-dione (4), together with one known compound mombasol (5) were isolated from the stem barks of *Aphanamixis grandifolia*. Their structures were elucidated on the basis of various spectroscopic analysis including electrospray ionization (ESI)-MS, high resolution (HR)-ESI-MS, IR, 1D- and 2D-NMR techniques (heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond connectivity (HMBC) and rotating frame Overhauser enhancement spectroscopy (ROESY)), and by comparison of their spectral data with those reported. The absolute configuration of compound 1 was determined by circular dichroism (CD) exciton chirality.

Key words *Aphanamixis grandifolia*; Meliaceae; nortriterpenoid

Species of the genus *Aphanamixis* (Meliaceae) are sources of various secondary metabolites with interesting diverse chemical structures. Previous chemical investigations on *Aphanamixis* have led to the isolation of a series of limonoids,[1—5] tirucallane triterpenoids,[6] diterpenoids,[7] sesquiterpenoids,[8] and flavone glycosides.[9] As a part of our continuous interest in the Meliaceae family,[10—12] four new tirucallane-type nortriterpenoids, 24,25-epoxy-tirucall-7,20(*E*)-diene-3,23-dione (**1**), 24,25,26,27-tetranortirucall-1,7-diene-23(21)-lactone (**2**), 3α-hydroxy-tirucall-7-ene-20-one (**3**), and 3-oxo-tirucall-7-ene-3,20-dione (**4**), along with a known highly complex oxidized limonoid, mombasol (**5**),[13] were isolated from the EtOH exact of the stem barks of *Aphanamixis grandifolia* Bl., a timer tree mainly distributed in the tropical areas of Asia such as southern China, Malaysia, Indonesia and India.[14] In this paper, we describe the isolation and structural elucidation of these compounds.

Results and Discussion

Compound **1** was obtained as a white, amorphous powder. Its positive high resolution-electrospray ionization (HR-ESI)-MS showed a quasi-molecular ion at *m*/*z* 461.3028 $[M+Na]^+$ (Calcd for $C_{29}H_{42}O_3Na$, 461.3026), which indicated that it has a molecular formula of $C_{29}H_{42}O_3$ with nine degrees of unsaturation. The ^{1}H- and ^{13}C-NMR spectra (Table 1) exhib-



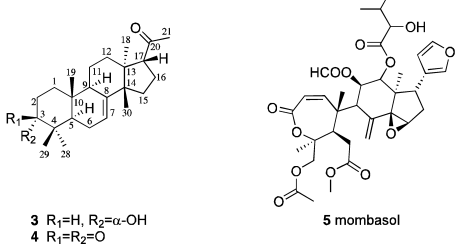


Table 1. ^{1}H- (500 MHz) and ^{13}C-NMR (125 MHz) Spectral Data of **1** and **2** in $CDCl_3$ (δ in ppm)

No.	**1**		**2**	
	δ_C	δ_H (multi, *J* in Hz)	δ_C	δ_H (multi, *J* in Hz)
1α	38.5 (t)	1.45 (*)	154.7 (d)	6.88 (d, 10.4)
1β	—	1.98 (*)	—	—
2α	34.9 (t)	2.25 (dt, 14.5, 3.0)	125.9 (d)	5.91 (d, 10.4)
2β	—	2.75 (td, 14.5, 5.5)	—	—
3	216.5 (s)	—	204.7 (s)	—
4	47.9 (s)	—	44.3 (s)	—
5α	52.4 (d)	1.73 (*)	48.6 (d)	2.09 (*)
6α	24.4 (t)	2.11 (m)	23.6 (t)	2.09 (*)
6β	—	2.11 (m)	—	2.17 (m)
7	118.9 (d)	5.35 (dd, 6.5, 3.0)	119.9 (d)	5.43 (dd, 6.5, 2.5)
8	144.8 (s)	—	144.5 (s)	—
9α	48.4 (d)	2.29 (ddt, 13.0, 6.5, 3.0)	45.5 (d)	2.54 (*)
10	35.2 (s)	—	37.9 (d)	—
11α	17.5 (t)	1.62 (m)	17.8 (t)	1.70 (m)
11β	—	1.62 (m)	—	1.80 (m)
12α	30.5 (t)	1.48 (*)	31.9 (t)	1.48 (m)
12β	—	1.75 (*)	—	1.79 (m)
13	46.6 (s)	—	43.6 (s)	—
14	50.7 (s)	—	51.0 (s)	—
15α	34.7 (t)	1.65 (m)	34.4 (t)	1.61 (m)
15β	—	1.71 (*)	—	1.61 (m)
16α	26.7 (t)	1.72 (*)	27.3 (t)	1.35 (m)
16β	—	1.98 (*)		1.97 (m)
17β	51.2 (d)	2.57 (m)	51.0 (d)	1.79 (m)
18α	23.3 (q)	0.82 (s)	22.8 (q)	0.86 (s)
19β	12.7 (q)	1.02 (s)	13.5 (q)	1.04 (s)
20	152.1 (d)	7.05 (dd, 16.0, 7.5)	39.1 (d)	2.54 (*)
21a	—	—	72.3 (t)	4.38 (t, 8.5)
21b	—	—	—	3.93 (t, 9.0)
22	127.1 (d)	6.34 (dd, 16.0, 1.5)	34.6 (t)	2.54 (*)
23	194.9 (s)	—	176.8 (s)	2.20 (m)
24α	65.2 (d)	3.48 (s)	—	—
25	60.8 (s)	—	—	—
26α	24.8 (q)	1.45 (s)	—	—
27β	18.8 (q)	1.27 (s)	—	—
28α	24.6 (q)	1.05 (s)	24.2 (q)	1.13 (s)
29β	21.6 (q)	1.12 (s)	21.4 (q)	1.09 (s)
30β	27.3 (q)	1.05 (s)	27.7 (q)	1.07 (s)

* Signal pattern unclear due to overlapping.

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ited resonances for seven methyl groups [δ_H 0.82, 1.02, 1.05, 1.05, 1.12, 1.27 and 1.45 (each 3H, s); δ_C 23.3, 12.7, 24.6, 27.3, 21.6, 18.8, 24.8 (each q)], a trisubstituted double bond [δ_H 5.35 (1H, dd, J=6.5, 3.0 Hz); δ_C 118.9 (d), 144.8 (s)], an α,β-unsaturated ketone [δ_H 6.34 (1H, dd, J=16.0, 1.5 Hz, H-22), 7.05 (1H, dd, J=16.0, 7.5 Hz, H-20); δ_C 127.1 (d), 152.1 (d), 194.9 (s)] and a characteristic epoxy group [δ_H 3.48 (1H, s), δ_C 65.2 (d), 60.8 (s)] in addition to seven methylene carbons, seven methine carbons, and eight quaternary carbons. The four olefinic carbons, two ketone carbons, and one epoxy ring account for five degrees of unsaturation. The remaining four degrees of unsaturation suggested that the molecule contains four rings in core carbon skeleton. After assignment of all the protons to their directly bonded carbons from heteronuclear single quantum coherence (HSQC), the total structural skeleton of **1** was established by heteronuclear multiple bond connectivity (HMBC) and rotating frame Overhauser enhancement spectroscopy (ROESY) correlations. The connectivity of Me-18 to C-13, Me-19 to C-10, Me-28 and Me-29 to C-4 and Me-30 to C-14 were determined from the following HMBC long-range correlations (Fig. 1): Me-18 at δ_H 0.82 with C-12, C-14 and C-17; Me-19 at δ_H 1.02 with C-1, C-5 and C-9; Me-30 at δ_H 1.05 with C-8 and C-15; and two *gem*-dimethyl (Me-28 and Me-29) at δ_H 1.05 and 1.12 with a ketone carbonyl (C-3) at δ_C 216.5. These data suggested **1** has a 3-oxo-Δ^7-tetracyclic skeleton.[15,16] The NMR spectra (Table 1) of **1** were similar to that of **1a**,[17] with the major differences being the loss of a doublet methyl carbon in side-chain and instead, the appearances of a *trans*-double bond and an upfield shifted carbonyl carbon signal at δ_C 194.9 (C-23), suggesting the existence of an α,β-unsaturated ketone in the side-chain of **1**, which was confirmed by the HMBC correlations observed from the two olefinic protons (H-20 and H-22) to the carbonyl carbon (C-23), placing the *trans*-double bond at C-20 and C-22. The HMBC cross-peaks from the epoxylated singlet proton at δ_H 3.48 to C-23, C-25 and two terminal methyl signals (C-26 and C-27) assigned a 24,25-epoxy group in the side-chain. The linkage of the side-chain to the tetracyclic core skeleton between C-17 and C-20 was also confirmed by HMBC correlation between H-20 and C-17. The planar structure of **1** was thus established as shown.

The relative configuration of **1** was determined by a ROESY experiment (Fig. 2). The ROESY correlations of H-5 with H-9 and Me-28, and Me-18 with H-9 and Me-26 (δ_H 1.45), indicated that H-5, H-9, Me-18, Me-26 and Me-28 were confacial and arbitrarily assigned as α-oriented. The ROESY correlation between H-24 and Me-26 assigned an α-orientation to H-24, thus the β-orientation to the 24,25-epoxy group, which was also consistent with that of cordialin A acetate, a compound with similar side-chain, confirmed by X-ray analysis.[18] The nuclear Overhauser effect (NOE) correlations between H-17 and Me-30 helped the determination of H-17 as β-orientated. The structure of **1** was thus established as 24,25-epoxy-tirucall-7,20 (*E*)-diene-3,23-dione.

The absolute configuration of **1** (Fig. 3) was determined by

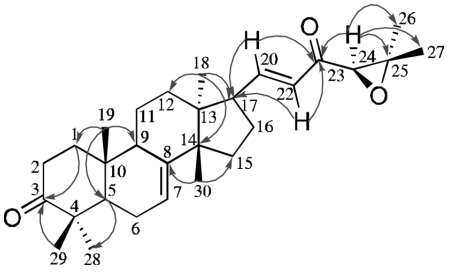

Fig. 1. Key HMBC (H→C) Correlations of **1**

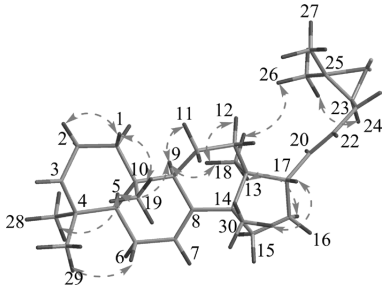

Fig. 2. Selected ROESY Correlations of **1**

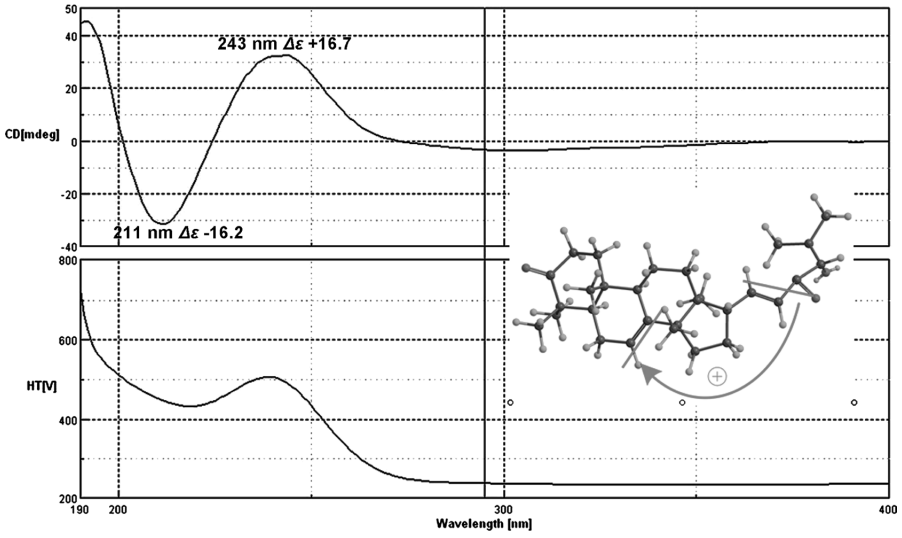

Fig. 3. CD and UV Spectra of **1**

Bold lines denote the electrictransition dipole of the chromophores.

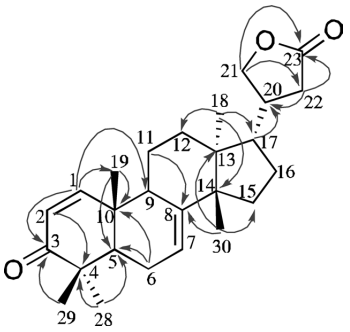

Fig. 4. Key HMBC (H→C) Correlations of **2**

the circular dichroism (CD) exciton chirality method. The CD spectrum of **1** revealed a negative Cotton effect at λ_{max} 211 nm ($\Delta\varepsilon$ −16.2) and a positive Cotton effect at λ_{max} 243 nm ($\Delta\varepsilon$ +16.7) due to the transition interaction between two different chromophores of the $\Delta^{7(8)}$ double bond[19] and α,β-unsaturated ketone,[20] indicating a positive chirality for **1**, thus determined the absolute configuration as depicted.

Compound **2** had the molecular formula $C_{26}H_{36}O_3$ as inferred from its high resolution mass spectrum, indicating nine degrees of unsaturation. The IR spectrum showed two strong absorption bands due to carbonyl (1782 cm^{-1}) and double bond (1675 cm^{-1}). The ^{13}C-NMR spectrum resolved 26 carbon resonances, classified into five methyls, seven methylenes (one oxygenated), seven methines (three olefinic carbons), and seven quaternary carbons (two carbonyl and one olefinic carbons) with the help of HSQC experiment. The aforementioned NMR data indicated that four out of the seven degrees of unsaturation come from two carbon–carbon double bonds and two carbonyls. The remaining five degrees of unsaturation required **2** to comprise five rings. The NMR spectra of **2** exhibited the characteristic signals of an α,β-unsaturated ketone [δ_H 6.88 (1H, d, J=10.4 Hz) and 5.91 (1H, d, J=10.4 Hz), δ_C 154.7 (d), 125.9 (d) and 204.7 (s)]. This unit was confirmed by the HMBC correlations (Fig. 4) from the two down-field shifted olefinic protons to the ketone carbon signal at δ_C 204.7, which showed cross-peaks with the two *gem*-methyl protons at δ_H 1.13 and 1.09 (each 3H, s), suggesting the presence of a ketone group at C-3 position and thus an α,β-unsaturated ketone structure in ring A. Both the *gem*-dimethyl and the C-3 signals correlated in the HMBC spectrum to the carbon signal at δ_C 48.6, coupled to a methine signal at δ_H 2.09 in the HSQC spectrum and is, hence, assigned to C-5, which in turn exhibited correlation with the olefinic proton (H-7). A γ-lactone nature of the side-chain and its position at C-17 were suggested by the HMBC long-range cross-peaks from protons at δ_H 4.38 (1H, t, J=8.5 Hz, H-21a) and 3.93 (1H, t, J=9.0 Hz, H-21b) to C-17, C-20 and C-23, and from H-17 to C-20 and C-22. Comprehensive analysis of the 2D-NMR data, especially HMBC (Fig. 4), allowed the establishment of the planar structure of **2**, similar to **2a**[21] with a saturated ketone in ring A. The relative configurations of **2** were determined to be the same as those of **2a** by ROESY spectrum in a way similar to **1**. Therefore, the whole structure of **2** was established as depicted.

Compound **3** gave a molecular formula of $C_{24}H_{38}O_2$ (six degrees of unsaturation), established by the HR-ESI-MS

Table 2. ^{1}H- (500 MHz) and ^{13}C-NMR (125 MHz) Spectral Data of **3** and **4** in $CDCl_3$ (δ in ppm)

No.	**3**		**4**	
	δ_C	δ_H (multi, J in Hz)	δ_C	δ_H (multi, J in Hz)
1α	31.2 (t)	1.48 (m)	38.4 (t)	1.47 (td, 14.0, 4.0)
1β	—	1.37 (m)	—	2.00 (ddd, 14.0, 5.5, 4.0)
2α	25.4 (t)	1.63 (*)	34.8 (t)	2.25 (*)
2β	—	1.93 (*)	—	2.76 (td, 14.5, 5.5)
3β	76.2 (d)	3.46 (t, 2.8)	216.4 (s)	—
4	37.4 (s)	—	47.8 (s)	—
5α	44.6 (d)	1.77 (*)	52.2 (d)	1.73 (*)
6α	23.9 (t)	1.95 (*)	24.3 (t)	2.10 (*)
6β	—	2.05 (m)	—	2.10 (*)
7	119.1 (d)	5.29 (dd, 6.5, 3.5)	119.0 (d)	5.35 (dd, 6.5, 3.5)
8	144.5 (s)	—	144.3 (s)	—
9α	48.3 (d)	2.33 (m)	48.1 (d)	2.28 (*)
10	34.8 (s)	—	35.1 (s)	—
11α	17.5 (t)	1.59 (m)	17.7 (t)	1.67 (m)
11β	—	1.68 (m)	—	1.67 (m)
12α	32.5 (t)	1.76 (*)	32.3 (t)	1.79 (m)
12β	—	2.08 (m)	—	2.12 (*)
13	45.0 (s)	—	44.9 (s)	—
14	51.7 (s)	—	51.6 (s)	—
15α	34.0 (t)	1.62 (*)	34.0 (t)	1.60 (m)
15β	—	1.54 (m)	—	1.60 (m)
16α	21.9 (t)	1.72 (m)	21.9 (t)	1.74 (*)
16β	—	2.26 (m)	—	2.27 (*)
17β	61.6 (d)	2.82 (dd, 9.0, 8.5)	61.5 (d)	2.83 (dd, 9.0, 8.5)
18α	23.2 (q)	0.76 (s)	23.2 (q)	0.75 (s)
19β	13.0 (q)	0.80 (s)	12.7 (q)	1.03 (s)
20	210.0 (s)	—	209.7 (s)	—
21	31.0 (q)	2.11 (s)	30.9 (q)	2.12 (s)
28α	27.8 (q)	0.93 (s)	24.5 (q)	1.05 (s)
29β	21.8 (q)	0.92 (s)	21.5 (q)	1.12 (s)
30β	27.1 (q)	1.05 (s)	27.2 (q)	1.08 (s)

* Signal pattern unclear due to overlapping.

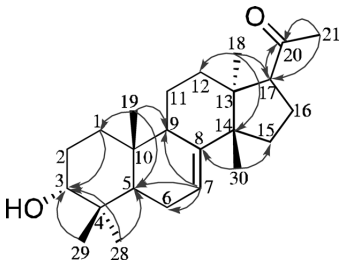

Fig. 5. Key HMBC (H→C) Correlations of **3**

pseudo-molecular ion at m/z 381.2769 $[M+Na]^+$ (Calcd for $C_{24}H_{38}O_2Na$, 381.2764). The ^{1}H- and ^{13}C-NMR of **3** (Table 2) showed 24 signals for six tertiary methyls (δ_C 13.0, 21.8, 23.2, 27.1, 27.8, and 31.0), seven methylenes, five methines (one oxygenated), and six quaternary carbons (one carbonyl carbon δ_C 210.0). Among them, signals of one downfield shifted methyl protons at δ_H 2.11 (3H, s), indicating the presence of a vicinal carbonyl carbon, two olefinic carbons [δ_H 5.29 (1H, dd, J=6.5, 3.5 Hz); δ_C 119.1 (d), 144.5 (s)], and one oxymethine carbon [(δ_H 3.46 (1H, t, J=2.8 Hz); δ_C 76.2 (d)] were observed. These data featured a tirucallane-type triterpenoids with a double bond between C-7 and C-8, and a 3α-hydroxy.[16]

The HMBC correlations (Fig. 5) of H-3 (δ_H 3.46) with C-1, C-2 and C-5 confirmed the position of the OH at C-3. The

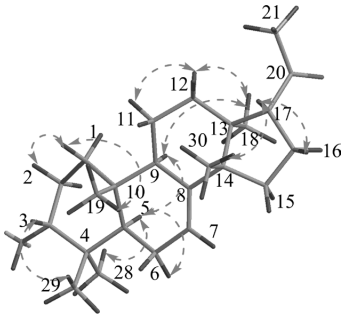

Fig. 6. Selected ROESY Correlations of **3**

correlations from an olefinic proton (δ_H 5.29, H-7) to C-5, C-6, and C-9 suggested a Δ^7 double bond. The presence of the tetracyclic core skeleton was supported by the HMBC cross-peaks from Me-18 to C-13, C-14 and C-17, Me-19 to C-1, C-5, C-9 and C-10, from both the *gem*-dimethyl (Me-28 and Me-29) to C-3, C-4 and C-5, Me-28 to C-29, and Me-29 to C-28. The key correlations from a methyl (δ_H 2.11, H-21) to C-17 and C-20, and from H-17 to C-20 clarified the side-chain and its linkage to the tetracyclic core between C-17 and C-20.

The relative configuration of the triterpenoid core was mainly established by a ROESY experiment (Fig. 6). The cross-peaks of Me-28 with H-5, H-5 with H-9, Me-18 with H-9, Me-18 with H-12α and Me-18 with H-16α, indicated that they were confacial and were randomly assigned as α-orientation. The ROESY correlations between Me-29 and H-3, Me-30 and H-17 revealed that H-3, H-17, Me-29 and Me-30 were in β-orientation, and further confirmed the α configuration of the OH-3. The structure of **3** was thus established as 3α-hydroxy-tirucall-7-ene-20-one.

Compound **4** was obtained as a white amorphous powder with a molecular formula of $C_{24}H_{36}O_2$ (seven drgees of unsaturation) in agreement with the HR-ESI-MS analysis (*m/z* 379.2609 $[M+Na]^+$, Calcd for $C_{24}H_{36}O_2Na$, 379.2608), one more degree of unsaturation compared to compound **3**. The ^{1}H- and ^{13}C-NMR data for **4** were similar to those of **3** (Table 2), especially in rings B, C and D and the side-chain. The major difference was the appearance of a carbonyl carbon signal at δ_C 216.4 in **4** instead of the signal of 3-OH in **3**, and as a consequence, a characteristic downfield shifted its vicinal methylene [(δ_H 2.76 (1H, td, J=14.5, 5.5 Hz), 2.25 (1H, signal overlapping); δ_C 34.8)], thus identified the structure of **4** as 3-oxo-tirucall-7-ene-3,20-dione.

Tetranortritrpenoids exemplified by compound **5** distributed widely in the genus *Aphanamixis*, while tirucallane-type nortriterpenoids were seldom encountered. It is noteworthy that compound **1** was the first tirucallane-type nortriterpenoids with the loss of the C-21 methyl, forming a *trans*-double bond at C-20 and C-22. Compound **2** featured a γ-lactone in side-chain and an α,β-unsaturated ketone in ring A, which was also scarce in tetranortriterpenoids. Compounds **3** and **4** were C_{24} tirucallane triterpenoids formed by degradation of six carbons in the side-chain, which have never been reported as natural products.[22)]

Experimental

General Procedures Optical rotations were determined with a *JASCO* P-1020 polarimeter (Na filter, λ=589 nm) in $CHCl_3$ solution. IR spectra were recorded on a Bruker Tensor 27 spectrometer with KBr-disks. Mass spectra were obtained on a MS Agilent 1100 Series LC/MSD Trap mass spectrometer (ESI-MS) and HR-ESI-MS was done on a Mariner time-of-flight mass spectrometer with an electrospray interface, respectively. NMR spectra were recorded on Bruker ACF-500 NMR instrument (^{1}H: 500 MHz, ^{13}C: 125 MHz) with tetramethylsilane (TMS) as internal standard. Silica gel (200—300 mesh, Qingdao Haiyang Chemical Co., Ltd., China), Sephadex LH-20 (Pharmacia, U.S.A.), and RP-C_{18} (40—63 μm, YMC, U.S.A.) were used for column chromatography. Preparative HPLC was carried out using Shimadzu with a Shimpak RP-C_{18} column (20×200 mm, i.d.) and Multiple Wavelength detector. All solvents used were of analytical grad (Jiangsu Hanbang Sci. & Tech. Co., Ltd., China). Fractions were monitored by TLC. Spots were visualized by heating silica gel plates immersed in vanillin–H_2SO_4 in ethanol.

Plant Material The stem barks of *Aphanamixis grandifolia* Bl. were collected from Xishuangbanna, Yunnan Province, China in May 2008, and authenticated by Prof. Jingyun Cui of Xishuangbanna Tropical Garden, Chinese Academy of Sciences. A Voucher Specimen (No. AG-200805) has been deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University.

Extraction and Isolation Air-dried stem barks of the plant material (10 kg) were extracted with 95% EtOH three times. The solvent was evaporated *in vacuo*, and the extracts were combined and concentrated, followed by suspension in water. The water layer was further extracted with $CHCl_3$ and EtOAc. The $CHCl_3$ fraction (350 g) was fractionated by column chromatography over D101 porous resin using gradient aqueous ethanol to give five fractions (fractions I—V).

Fraction I (15 g) was chromatographed on a RP-18 Si gel and eluted with MeOH–H_2O (4 : 6—1 : 0, v/v) under grandient conditions, yielding five fractions (IA—IE). The fifth fraction IE (2.2 g) was fractioned into three parts over RP-18 Si gel with MeOH–H_2O again, then fraction IEA (548 mg) was further purified on sephadex LH-20 (EtOAc–MeOH 1 : 1, v/v) and applied to a RP-18 Si gel column (eluted with acetone–H_2O 3 : 7, v/v) to yield **5** (15 mg).

Fraction II (150 g) was fractionated to 11 fractions using chromatography on silica gel eluted with 0—10% MeOH in CH_2Cl_2. The third fraction IIC (30 g) was separated eight fractions over RP-18 Si gel and eluted with MeOH–H_2O (6 : 4—1 : 0) under gradient conditions. Then, the fraction IICB (15 g) was chromatographed on a Si gel column eluted with a mixture of petroleum ether–EtOAc (25 : 1—2 : 1, v/v) in gradient to give seven major fractions. Fraction IICBC (2.18 g) was separated over a reversed-phase Si gel column (MeOH–H_2O, 80 : 20, v/v) to afford three major fractions, IICBC 1 (241 mg), IICBC 2 (925 mg), and IICBC 3 (524 mg). Fractions IICBC 1—IICBC 3 were respectively purified by column chromatography over Sephadex LH-20 (CH_2Cl_2–MeOH, 1 : 1, v/v). Finally, the fraction IICBC 2 (530 mg) was further purified by successive RP-18 preparative HPLC with MeOH–H_2O (85%, v/v) to obtain **2** (16.9 mg, t_R 22.8 min) and **3** (5.5 mg, t_R 24.3 min), the fraction IICBC 3 (446 mg) was then subjected to preparative HPLC with CH_3CN–H_2O (88%, v/v) to yield **4** (12.7 mg, t_R 19.5 min). Fraction IICBD (3.5 g) was subjected to a Si gel column eluted with a mixture of petroleum ether–EtOAc (8 : 1, v/v) to afford two fractions, IICBD 1 (950 mg), and IICBD 2 (713 mg). Fraction IICBD 1 was purified by reversed-phase octadecyl silica gel (ODS) and Sephadex LH-20 (CH_2Cl_2–MeOH, 1 : 1, v/v) chromatography and then subjected to preparative HPLC to yield **1** (14.3 mg, t_R 20.4 min) with MeOH–H_2O (90%, v/v).

24,25-Epoxy-tirucall-7,20(*E*)-diene-3,23-dione (**1**): White, amorphous powder; $[\alpha]_D^{27}$ −2.1 (c=0.73, $CHCl_3$); CD λ_{max} (c=0.72, CH_3CN) nm ($\Delta\varepsilon$): 191 (+23.4), 211 (−16.2), 243 (+16.7); IR (KBr) ν_{max} cm^{-1}: 3447, 2967, 2866, 2351, 2320, 1708, 1682, 1622, 1456, 1387, 648; ^{1}H- and ^{13}C-NMR spectral data: see Table 1; ESI-MS *m/z* 461.3 $[M+Na]^+$, 899.6 $[2M+Na]^+$; HR-ESI-MS *m/z* 461.3028 $[M+Na]^+$ (Calcd for $C_{29}H_{42}O_3Na$, 461.3026).

24,25,26,27-Tetranortirucall-1,7-diene-23(21)-lactone (**2**): White, amorphous powder; $[\alpha]_D^{27}$ −2.1 (c=0.19, $CHCl_3$); IR (KBr) ν_{max} cm^{-1} 3454, 2961, 2878, 1783, 1707, 1675, 1474, 1382, 1366, 1179, 1038, 1019, 827, 717, 657; ^{1}H- and ^{13}C-NMR see Table 1; HR-ESI-MS *m/z* 419.2570 $[M+Na]^+$ (Calcd for $C_{26}H_{36}O_3Na$, 419.2557).

3α-Hydroxy-tirucall-7-ene-20-one (**3**): White, amorphous powder; $[\alpha]_D^{27}$ −94.1 (c=0.35, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3557, 3523, 2964, 2939, 2879, 2841, 2353, 2320, 1698, 1471, 1385, 1362, 1209, 1183, 1040, 829, 644; ^{1}H- and ^{13}C-NMR spectral data: see Table 2; ESI-MS *m/z* 359.3 $[M+H]^+$; HR-ESI-MS *m/z* 381.2769 $[M+Na]^+$ (Calcd for $C_{24}H_{38}O_2Na$, 381.2764).

3-Oxo-tirucall-7-ene-3,20-dione (**4**): White, amorphous powder; $[\alpha]_D^{27}$ −161.9 (c=0.11, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3445, 2965, 2882, 2352, 1786, 1706, 1642, 1472, 1387, 1360, 1205, 1172, 650, 581; ^{1}H- and ^{13}C-

NMR spectral data: see Table 2; ESI-MS *m*/*z* 379.2 $[M+Na]^+$, 735.5 $[2M+Na]^+$; HR-ESI-MS *m*/*z* 379.2609 $[M+Na]^+$ (Calcd for $C_{24}H_{36}O_2Na$, 379.2608).

Mobasol (**5**): White, amorphous powder; ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H: 6.94 (1H, d, *J*=12.9 Hz, H-1), 6.32 (1H, d, *J*=12.9 Hz, H-2), 3.42 (1H, d, *J*=8.1 Hz, H-5), 2.40 (1H, d, *J*=9.0 Hz, H-6a), 2.28 (1H, d, *J*=14.1 Hz, H-6b), 3.12 (1H, d, *J*=7.5 Hz, H-9), 5.76 (1H, dd, *J*=11.0, 7.5 Hz, H-11), 6.02 (1H, d, *J*=11.0 Hz, H-12), 3.91 (1H, s, H-15), 1.84 (1H, dd, *J*=14.0, 10.8 Hz, H-16α), 2.28 (1H, dd, *J*=14.0, 6.9 Hz, H-16β), 3.07 (1H, dd, *J*=10.5, 6.9 Hz, H-17), 0.94 (3H, s, H-18), 1.00 (3H, s, H-19), 7.11 (1H, s, H-21), 6.14 (1H, s, H-22), 7.33 (1H, s, H-23), 1.34 (3H, s, H-28), 4.68 (1H, d, *J*=11.7 Hz, H-29a), 4.35 (1H, d, *J*=11.7 Hz, H-29b), 5.40 (1H, s, H-30a), 5.27 (1H, s, H-30b), 1.23 (1H, m, H-3′), 1.35 (2H, m, H-4′), 0.68 (3H, d, *J*=6.3 Hz, H-5′), 0.82 (3H, t, *J*=7.2, 6.9 Hz, H-6′), 8.07 (1H, s, HCOOR), 3.73 (3H, s, OMe) and 2.10 (3H, s, OAc). ^{13}C-NMR (125 MHz, $CDCl_3$) δ_C: 147.4 (C-1), 122.7 (C-2), 165.4 (C-3), 84.0 (C-4), 50.4 (C-5), 34.7 (C-6), 173.1 (C-7), 136.1 (C-8), 53.2 (C-9), 45.4 (C-10), 69.8 (C-11), 72.9 (C-12), 46.0 (C-13), 70.8 (C-14), 59.7 (C-15), 33.8 (C-16), 37.6 (C-17), 12.6 (C-18), 23.7 (C-19), 121.7 (C-20), 140.4 (C-21), 111.0 (C-22), 142.7 (C-23), 24.6 (C-28), 63.8 (C-29), 121.5 (C-30), 175.0 (C-1′), 75.2 (C-2′), 37.8 (C-3′), 26.2 (C-4′), 11.7 (C-5′), 13.5 (C-6′), 159.7 (HCOOR), 52.5 (OMe), 20.7 (OAc-Me) and 170.3 (OAc-CO). ESI-MS *m*/*z* 721.6 $[M+Cl]^-$; 687.2 $[M+H]^+$, 704.3 $[M+NH_4]^+$ and 709.3 $[M+Na]^+$.

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