Five New Tetranortriterpenoids from the Seeds of *Toona ciliata*

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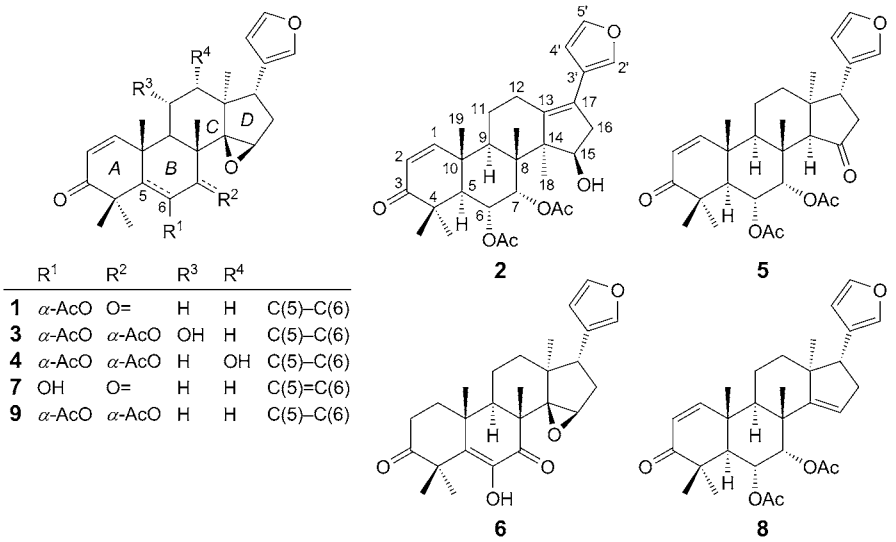
Five new tetranortriterpenoids, toonaciliatones B–F (**1**–**5**, resp.), together with four known compounds, dihydrocedrelone (**6**), cedrelone (**7**), 6α-acetoxyazadirone (**8**), and 6α-acetoxy-14β,15β-epoxyazadirone (**9**), were isolated from the seeds of *Toona ciliata*. Their structures were elucidated by spectroscopic methods, including 1D- and 2D-NMR spectroscopy.

Introduction. – Plants of the Meliaceae family are rich sources of limonoids which are structurally diverse and biologically significant [1]. *Toona ciliata* ROEM. var. *ciliata* (Meliaceae) is a timber tree mainly growing in the tropical areas of Asia such as India, Malaysia, Indonesia, and Southern China [2]. The bark has been used to treat dysentery, fever, and menstrual disorders in Chinese folk medicine [3]. Limonoids [4], norlimonoids [5], and coumarins [6] were reported as the main constitutents in the stem and leaves of *T. ciliata.* However, only a few chemical investigations about the seeds of *T. ciliata* have been reported. In consideration of the use of these bioactive metabolites, it seemed necessary to study the components from the seeds of *T. ciliata.*

Here, we report on the constituents of the 95% MeOH extract of the seeds of *T. ciliata*, from which five new compounds, named toonaciliatones B–F (**1**–**5**, resp.), and four known tetranortriterpenoids, dihydrocedrelone (**6**) [7], cedrelone (**7**) [8], 6α-acetoxyazadirone (**8**) [9], 6α-acetoxy-14β,15β-epoxyazadirone (**9**) [4b] were isolated (*Fig. 1*). The structures of the compounds were determined by 1D- and 2D-NMR spectroscopy, and by comparison with the data of related known compounds.

Results and Discussion. – Repeated chromatography over SiO_2 and *Sephadex LH-20*, and semipreparative HPLC of the 95% MeOH extract of the seeds of *T. ciliata* yielded five new compounds, **1**–**5**, and four known ones, **6**–**9**.

Compound **1**, obtained as a white powder, was assigned the molecular formula $C_{28}H_{34}O_6$ by HR-ESI-MS (*m*/*z* 489.2248 ($[M+Na]^+$; calc. 489.2253)), which indicated twelve degrees of unsaturation. The ^{1}H-NMR spectrum (*Table 1*) contained five Me *singlet*s at δ(H) 0.80, 1.26, 1.34, 1.29, and 1.28, one *singlet* for an AcO group at δ(H) 2.24, five signals for olefinic H-atoms at δ(H) 7.18 (H–C(1)), 6.01 (H–C(2)), 7.15 (H–C(2′)), 6.17 (H–C(4′)), and 7.48 (H–C(5′)), and five CH and three CH_2 signals. The ^{13}C-NMR (*Table 2*) displayed 28 C-atom signals which were classified by a DEPT experiment into those for five Me (δ(C) 18.7, 20.0, 21.7, 23.9, and 31.5), one AcO (δ(C)



	R^1	R^2	R^3	R^4	
1	α-AcO	O=	H	H	C(5)–C(6)
3	α-AcO	α-AcO	OH	H	C(5)–C(6)
4	α-AcO	α-AcO	H	OH	C(5)–C(6)
7	OH	O=	H	H	C(5)=C(6)
9	α-AcO	α-AcO	H	H	C(5)–C(6)

Fig. 1. *The structures of compounds* **1**–**9**

21.1), three CH_2 (δ(C) 19.2, 35.4, 32.2), and ten CH (δ(C) 156.5, 143.2, 139.6, 127.0, 110.9, 74.7, 56.9, 55.8, 46.7, and 41.9) groups (including two O-bearing and five olefinic CH groups), as well as nine quaternary C-atoms (including an α,β-unsaturated ketone, a ketone CO, and one olefinic C-atom). The ^{1}H- and ^{13}C-NMR data indicated **1** to be a tetranortriterpenoid. It was closely similar to 6α-acetoxy-14β,15β-epoxyazadirone (**9**). The difference between **9** and **1** was the presence of a C(7)=O group in **1** instead of a C(7)–OAc moiety in **9**. This was confirmed by the correlations from the signals of H–C(6), H–C(5), and Me–C(8) to the signal of the CO group at δ(C) 206.0 in the HMBC spectrum of **1**. The structure of **1** was deduced by the ^{1}H,^{1}H-COSY correlations and HMBCs shown in *Fig. 2*. Taken together, the structure of the new compound **1** was elucidated and it was named toonaciliatone B.

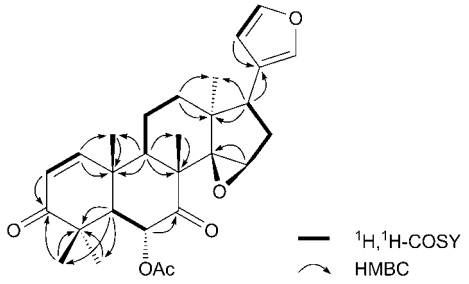


Fig. 2. *Key ^{1}H,^{1}H-COSY correlations and HMBCs of* **1**

The molecular formula of compound **2** was determined as $C_{30}H_{38}O_7$ by HR-ESI-MS (*m*/*z* 511.2704 ([$M+H$]$^+$; calc. 511.2696)). The ^{13}C-NMR and DEPT spectrum

Table 1. *^{1}H-NMR Data of* **1**–**5** (at 400, 600, and 500 MHz, resp.; in $CDCl_3$; δ in ppm, J in Hz)

	1[a])	**2**[b])	**3**[c])	**4**[c])	**5**[c])
H–C(1)	7.18 (*d*, *J* = 10.3)	7.10 (*d*, *J* = 10.1)	8.32 (*d*, *J* = 10.2)	7.17 (*d*, *J* = 10.2)	7.09 (*d*, *J* = 10.3)
H–C(2)	6.01 (*d*, *J* = 10.3)	5.92 (*d*, *J* = 10.1)	5.85 (*d*, *J* = 10.2)	5.95 (*d*, *J* = 10.0)	5.94 (*d*, *J* = 10.3)
H–C(5)	2.38 (*d*, *J* = 10.1)	2.65 (*d*, *J* = 12.3)	2.57 (*d*, *J* = 12.5)	2.51 (*d*, *J* = 12.3)	2.21 (*d*, *J* = 10.1)
H–C(6)	5.84 (*d*, *J* = 10.1)	5.40 (*dd*, *J* = 12.4, 2.2)	5.33 (*dd*, *J* = 12.5, 1.8)	5.35 (*d*, *J* = 12.3)	5.42 (*d*, *J* = 2.1)
H–C(7)	–	5.92 (*d*, *J* = 2.2)	4.98 (*d*, *J* = 1.9)	5.03 (*s*)	5.26 (*d*, *J* = 2.1)
H–C(9)	2.40–2.45 (*m*)	2.07 (*dd*, *J* = 12.7, 2.7)	2.85 (*d*, *J* = 10.6)	2.71 (*dd*, *J* = 13.1, 3.2)	1.28–1.32 (*m*)
CH_2(11) or H–C(11)	1.23–1.28 (*m*), 1.89–1.92 (*m*)	1.74–1.76 (*m*), 1.52–1.56 (*m*)	4.58–4.60 (*m*)	2.21–2.29 (*m*), 1.62–1.65 (*m*)	1.71–1.73 (*m*)
CH_2(12) or H–C(12)	1.64–1.69 (*m*), 2.05–2.07 (*m*)	2.80 (*dd*, *J* = 6.4, 2.3), 2.07 (*dd*, *J* = 12.7, 2.7)	2.43 (*d*, *J* = 5.7), 1.64 (*d*, *J* = 11.2)	4.31 (*dd*, *J* = 12.9, 2.9)	1.35–1.41 (*m*), 2.03–2.06 (*m*)
H–C(14)	–	–	–	–	2.54 (*s*)
H–C(15)	3.51 (*d*, *J* = 1.0)	4.42 (*dd*, *J* = 8.5, 3.5)	3.49 (*s*)	3.43 (*s*)	
CH_2(16)	1.94–1.96 (*m*), 2.40–2.45 (*m*)	2.77 (*d*, *J* = 2.5), 2.65 (*d*, *J* = 12.3)	2.17 (*dd*, *J* = 10.4, 5.5), 1.62 (*dd*, *J* = 10.2, 8.2)	2.27–2.31 (*m*), 1.66–1.71 (*m*)	2.54 (*d*, *J* = 10.0)
H–C(17)	2.71–2.74 (*m*)	–	2.65 (*dd*, *J* = 10.5, 6.2)	2.86 (*dd*, *J* = 10.5, 6.0)	3.46 (*d*, *J* = 10.0)
Me(18)	0.80 (*s*)	1.23 (*s*)	1.07 (*s*)	1.07 (*s*)	1.12 (*s*)
Me(19)	1.26 (*s*)	1.15 (*s*)	1.25 (*s*)	1.19 (*s*)	1.15 (*s*)
H–C(2′)	7.15 (*s*)	7.39 (*s*)	7.12 (*s*)	7.23 (*s*)	7.26 (*d*, *J* = 10.2)
H–C(4′)	6.17 (*s*)	6.48 (*s*)	6.17 (*s*)	6.33 (*s*)	6.26 (*s*)
H–C(5′)	7.48 (*s*)	7.40 (*s*)	7.38 (*s*)	7.39 (*s*)	7.39 (*d*, *J* = 10.2)
Me_β–C(4)	1.34 (*s*)	1.25 (*s*)	1.23 (*s*)	1.16 (*s*)	1.68 (*s*)
Me_α–C(4)	1.29 (*s*)	1.39 (*s*)	1.27 (*s*)	1.25 (*s*)	1.28 (*s*)
Me–C(8)	1.28 (*s*)	1.09 (*s*)	1.36 (*s*)	1.59 (*s*)	1.24 (*s*)
Me of AcO	2.24 (*s*)	2.01 (*s*), 2.17 (*s*)	2.01 (*s*), 2.13 (*s*)	2.15 (*s*), 2.02 (*s*)	2.14 (*s*), 2.03 (*s*)

[a]) Recorded at 400 MHz. [b]) Recorded at 600 MHz. [c]) Recorded at 500 MHz.

Table 2. *^{13}C-NMR and DEPT Data of* **1**–**5** (at 100, 150, and 125 MHz, resp.; in $CDCl_3$; δ in ppm)

	1[a])	**2**[b])	**3**[c])	**4**[c])	**5**[c])
H–C(1)	156.5 (*d*)	158.4 (*d*)	162.3 (*d*)	157.4 (*d*)	157.3 (*d*)
H–C(2)	127.0 (*d*)	125.8 (*d*)	124.2 (*d*)	126.5 (*d*)	126.3 (*d*)
C(3)	203.0 (*s*)	204.5 (*s*)	204.6 (*s*)	204.8 (*s*)	204.7 (*s*)
C(4)	40.2 (*s*)	40.6 (*s*)	41.5 (*s*)	47.4 (*s*)	46.7 (*s*)
H–C(5)	56.9 (*d*)	41.6 (*d*)	47.7 (*d*)	48.5 (*d*)	45.8 (*d*)
H–C(6)	74.7 (*d*)	70.0 (*d*)	70.0 (*d*)	70.3 (*d*)	68.9 (*d*)
C(7) or H–C(7)	206.0 (*s*)	77.1 (*d*)	73.3 (*d*)	73.1 (*d*)	72.9 (*d*)
C(8)	47.0 (*s*)	44.8 (*s*)	45.5 (*s*)	42.5 (*s*)	43.0 (*s*)
H–C(9)	46.7 (*d*)	46.5 (*d*)	44.1 (*d*)	39.1 (*d*)	44.9 (*d*)
C(10)	52.6 (*s*)	46.6 (*s*)	41.6 (*s*)	40.4 (*s*)	40.5 (*s*)
CH_2(11) or H–C–(11)	19.2 (*t*)	22.2 (*t*)	68.0 (*d*)	29.4 (*t*)	18.0 (*t*)
CH_2(12) or H–C–(12)	35.4 (*t*)	23.6 (*t*)	44.2 (*t*)	72.4 (*d*)	34.3 (*t*)
C(13)	42.2 (*s*)	141.2 (*s*)	42.3 (*s*)	45.3 (*s*)	41.2 (*s*)
C(14)	67.0 (*s*)	56.7 (*s*)	73.1 (*s*)	72.6 (*s*)	61.4 (*s*)
H–C(15)	55.8 (*d*)	82.2 (*d*)	57.9 (*d*)	56.8 (*d*)	217.9 (*s*)
CH_2(16)	32.2 (*t*)	43.8 (*t*)	32.1 (*t*)	33.4 (*t*)	42.1 (*t*)
H–C(17)	41.9 (*d*)	121.6 (*s*)	39.0 (*d*)	39.3 (*d*)	37.8 (*d*)
Me(18)	20.0 (*q*)	27.3 (*q*)	21.3 (*q*)	15.2 (*q*)	27.9 (*q*)
Me(19)	18.7 (*q*)	17.0 (*q*)	20.0 (*q*)	21.3 (*q*)	21.3 (*q*)
H–C(2′)	139.6 (*d*)	140.1 (*d*)	139.6 (*d*)	140.5 (*d*)	140.2 (*d*)
C(3′)	123.5 (*s*)	120.9 (*s*)	123.3 (*s*)	123.8 (*s*)	122.5 (*s*)
H–C(4′)	110.9 (*d*)	109.5 (*d*)	110.8 (*d*)	111.9 (*d*)	110.7 (*d*)
H–C(5′)	143.2 (*d*)	142.9 (*d*)	143.7 (*d*)	143.5(*d*)	142.9 (*d*)
Me_{β}–C(4)	23.9 (*q*)	21.3 (*q*)	20.1 (*q*)	20.4 (*q*)	20.2 (*q*)
Me_{α}–C(4)	31.5 (*q*)	31.7 (*q*)	31.9 (*q*)	31.8 (*q*)	31.6 (*q*)
Me–C(8)	21.7 (*q*)	20.4 (*q*)	22.5 (*q*)	19.2 (*q*)	17.9 (*q*)
Me*C*OO	172.0 (*s*)	169.6 (*s*), 172.8 (*s*)	170.0 (*s*), 170.0 (*s*)	170.1 (*s*), 170.2 (*s*)	169.1 (*s*), 170.1 (*s*)
*Me*COO	21.1 (*q*)	21.2 (*q*), 21.9 (*q*)	21.2 (*q*), 21.3 (*q*)	21.5 (*q*), 21.8 (*q*)	21.1 (*q*), 21.1 (*q*)

[a]) Recorded at 100 MHz. [b]) Recorded at 150 MHz. [c]) Recorded at 125 MHz.

(*Table 2*) showed 30 signals of C-atoms assignable to three CO groups (including an α,β-unsaturated ketone (δ(C) 204.5) and two AcO CO groups (δ(C) 169.6, 172.8)), a tetrasubstituted C=C bond (δ(C) 141.2, 121.6), five Me, one AcO Me, three CH_2, five CH (including one HO-bearing CH group (δ(C) 82.2) and two AcO-bearing CH groups (δ(C) 70.0, 77.1)), and five olefinic CH groups, as well as five quaternary C-atoms (including one olefinic C-atom). These data suggested that **2** is a tetranortripenoid possessing the same *A*, *C*, and *D* rings as the known compound isocedrelone acetate [10]. In the *B* ring, C(7) was substituted by an α-AcO group in **2** instead of the C(7)=O group.

Correlations from the signal of H–C(6) to those of C(5), C(4), C(8), and a CO group (δ(C) 169.6) and from the signal of H–C(7) to those of C(5), C(8), C(9), and a

CO group (δ(C) 172.8) were observed in the HMBC spectrum of **2**. The relative orientations of the two AcO groups were deduced from the ROESY spectrum. The NOE interactions of the signal of H–C(7) with that of the β-oriented Me–C(8) and those of H–C(6) with the H–C(7) signal suggested that the two AcO groups located at C(6) and C(7) were α-oriented. Hence, **2** was established as toonaciliatone C.

Compound **3** displayed a molecular-ion peak at 527.2643 ($[M+H]^+$, $C_{30}H_{39}O_8^+$; calc. 527.2645) in the positive-ion mode HR-ESI-MS. The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*, resp.), HSQC, and HMBC spectra indicated that **3** was similar to **9**, except for the substitution pattern at C(11). The constitutional formula of **3** was determined on the basis of spectroscopic analyses and confirmed by ^{1}H,^{1}H-COSY and HMBC. The fragment CH(9)–CH(11)–CH_2(12) is positioned between C(8) and C(13) based on the observed ^{1}H,^{1}H-COSY correlations of the signal of H–C(11) with those of H–C(9) and H–C(12) and the HMBCs of the signal of H–C(11) with those of C(8), C(9), C(10), C(12), C(13), and C(18). The OH group was at C(11) taking into account the integral and the chemical shift of the H–C(11) signal. The relative orientation of the OH group was deduced as α from the interactions of the signal of H–C(11) with those of H–C(19) and Me–C(8) in the ROESY spectrum. Therefore, the structure of **3** was determined as depicted and named toonaciliatone D.

Compound **4** was isolated as colorless prisms and had the same molecular formula $C_{30}H_{38}O_8$ as **3**, determined by analysis of the 1D-NMR, DEPT, and HR-ESI-MS data (*m*/*z* 527.2647 ($[M+H]^+$, $C_{30}H_{39}O_8^+$; calc. 527.2645)). The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.) of **4** suggested that its structure was closely similar to that of **3**, except for the position of the OH group attached to ring *C*. The correlations of the signal of H–C(12) with those of H–C(11) and H–C(13) in the ^{1}H,^{1}H-COSY spectrum, and the correlations of the H–C(12) signal with those of C(11), C(13), and C(18) in the HMBC spectrum suggested that the OH group was at C(12). The relative orientation of the OH group at C(12) was deduced as α from the ROESY spectrum, where an interaction of the signal of H–C(12) with the one for H_β–C(17) was observed. Thus, **4** was elucidated as toonaciliatone E.

Compound **5** was obtained as a white power. The molecular formula was determined as $C_{30}H_{38}O_7$ by HR-ESI-MS (*m*/*z* 511.2704 ($[M+H]^+$; calc. 511.2696)). The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*, resp.) spectra of **5** revealed the presence of a furan ring, five Me groups, one C=C bond, and two AcO, and two ketone CO groups. Comparing the ^{1}H- and ^{13}C-NMR data of **5** with those of toonaciliatone A [11] showed similarities to this known compound, with the exception of two more AcO groups in **5**. The key HMBCs of the signals of H–C(6) (δ(H) 5.42)/C=O (δ(C) 170.1) and H–C(7) (δ(H) 5.26)/C=O (δ(C) 169.1) indicated that the two AcO groups were located at C(6) and C(7), respectively. The NOE interactions of the signal of H–C(7) with the one for Me_β–C(8) and the H–C(6) signal with the one of H–C(7) suggested that the relative orientations of both AcO groups were α. Thus, **5** was established as toonaciliatone F.

The four known compounds were identified as dihydrocedrelone (**6**) [7], cedrelone (**7**) [8], 6α-acetoxyazadirone (**8**) [9], and 6α-acetoxy-14β,15β-epoxyazadirone (**9**) [4b], by comparison of their spectroscopic data with literature data.

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Experimental Part

General. Anal. TLC: pre-coated silica-gel F_{254} plates (*Qingdao Marine Chemical Inc.*, P. R. China); spots were detected under UV light (254 and 365 nm), and by immerging in 10% aq. H_2SO_4 in H_2O, followed by heating. Column chromatography (CC): silica gel (SiO_2, 200–300 mesh; *Qingdao Marine Chemical Inc.*, P. R. China), *C-18* silica gel (40–75 mm; *Pharmacia Chemical Co.*), and *Sephadex LH-20* gel (*Pharmacia*). HPLC: *Agilent 1200*; semi-prep. column (*Zorbax SB-C18*, 9.4–250 mm, 5 mm); 2 ml/min. Optical rotations: *Jasco P-1020 Polarimeter* instrument. UV Spectra: *Shimadzu UV2401PC* spectrometer; λ_{max} (log ε) in nm. IR Spectra: *BRUKER Tensor-27* spectrophotometer; KBr pellets; in cm^{-1}. 1D- and 2D-NMR spectra: *BRUKER AV-400*, *BRUKER DRX-500*, and *Avance III 600* spectrometers; δ in ppm rel. to Me_4Si, J in Hz. MS: *VG Auto Spec-3000* mass spectrometer; in m/z. HR-ESI-MS: *API Qstar Pulsar LC/TOF* instrument; in m/z.

Plant Material. The seeds of *T. ciliata* were collected from Yuanmou County, Yunnan Province, P. R. China, in June 2010. The plant material was identified by Prof. *Hua Peng* (Botanical Garden, Kunming Institute of Botany, the Chinese Academy of Sciences). A voucher specimen (KIB-ZL-201007) has been deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried and powdered seeds of *T. ciliata* (6.0 kg) were exhaustively extracted with 95% MeOH (3×50 l) at r.t. under reflux. The MeOH extract was concentrated under reduced pressure. The residue was suspended in H_2O (10 l) and extracted with petroleum ether (PE; 3×10 l) and AcOEt (3×10 l). The AcOEt-soluble portion (147 g) was chromatographed on a SiO_2 column with PE/acetone 5:1 to yield one fraction (5.2 g), which gave a large, purple spot on TLC (PE/acetone 3:1; R_f 0.6) after immerging in 10% aq. H_2SO_4/H_2O and heating. This fraction was subjected to CC (*Sephadex LH-20*; MeOH) to give two fractions, *Frs. 1* and *2*. *Fr. 1* (2.0 g) was fractionated by CC (SiO_2; PE/acetone 10:1) to afford two fractions, *Frs. 1a* and *1b*. *Fr. 1b* was rechromatographed on a SiO_2 column with PE/acetone 30:1, followed by HPLC with a C_{18} semiprep. column with MeCN/H_2O (containing 0.05% TFA; 85:15) to yield compound **1** (t_R 11.14 min; 1 mg), as well as *dihydrocedrelone* (**6**), *cedrelone* (**7**), and *6α-acetoxyazadirone* (**8**). *Fr. 2* (2.8 g) was separated by CC (SiO_2; PE/acetone 10:1) to afford two fractions, *Frs. 2a* and *2b*. *Fr. 2a* was rechromatographed on a SiO_2 column with PE/acetone 20:1 to afford five fractions, *Frs. 2a1–2a5*. *Fr. 2* (0.72 g) was chromatographed on a *RP-18* SiO_2 column with MeOH/H_2O 80:20 to yield compound **2** (11.6 mg) and *6α-acetoxy-14β,15β-epoxyazadirone* (**9**). *Fr. 2a5* (0.37 g) was rechromatographed on a SiO_2 column with PE/acetone 20:1, to yield compounds **3** (4 mg), **4** (7 mg), and **5** (3.2 mg).

Toonaciliatone B (*=6α-Acetoxy-14β,15β:21,23-diepoxy-24,25,26,27-tetranorapotirucalla-1,20,22-triene-3,7-dione*; *(6α,13α,14β,15β,17α)-6-(Acetyloxy)-14,15-epoxy-17-(furan-3-yl)-4,4,8-trimethylandrost-1-ene-3,7-dione*; **1**). White powder. $[\alpha]_D^{16} = +1.3$ ($c = 0.4$, $CHCl_3$). UV (MeCN): 231 (3.92), 218 (4.23). IR (KBr): 1752, 1677. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (pos.): 489 ($[M+Na]^+$). HR-ESI-MS: 489.2248 ($[M+Na]^+$, $C_{28}H_{34}NaO_6^+$; calc. 489.2253).

Toonaciliatone C (*=6α,7α-Diacetoxy-21,23-epoxy-15β-hydroxy-24,25,26,27-tetranorapotirucalla-1,13(17),20,22-tetraen-3-one*; *(15β)-6,7-Bis(acetyloxy)-17-(furan-3-yl)-15-hydroxy-4,4,8,10,14-pentamethylgona-1,13(17)-dien-3-one*; **2**). White powder. $[\alpha]_D^{16} = +5.0$ ($c = 0.7$, $CHCl_3$). UV (MeCN): 240 (3.96), 219 (4.28). IR (KBr): 3504, 1743, 1674. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (pos.): 511 ($[M+H]^+$). HR-ESI-MS: 511.2704 ($[M+H]^+$, $C_{30}H_{39}O_7^+$; calc. 511.2696).

Toonaciliatone D (*=6α,7α-Diacetoxy-14β,15β:21,23-diepoxy-11α-hydroxy-24,25,26,27-tetranorapotirucalla-1,20,22-trien-3-one*; *(11α,13α,14β,15β,17α)-6,7-Bis(acetyloxy)-14,15-epoxy-17-(furan-3-yl)-11-*

hydroxy-4,4,8-trimethylandrost-1-en-3-one; **3**). White powder. $[\alpha]_D^{16} = +15.0$ ($c = 0.1$, $CHCl_3$). UV (MeCN): 231 (3.91), 218 (4.22). IR (KBr): 3446, 1745, 1674. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (pos.): 527 ($[M+H]^+$). HR-ESI-MS: 527.2643 ($[M+H]^+$, $C_{30}H_{39}O_8^+$; calc. 527.2645).

Toonaciliatone E (=*6α,7α-Diacetoxy-14β,15β:21,23-diepoxy-12α-hydroxy-24,25,26,27-tetranorapotirucalla-1,20,22-trien-3-one*; *(12α,13α,14β,15β,17α)-6,7-Bis(acetyloxy)-14,15-epoxy-17-(furan-3-yl)-12-hydroxy-4,4,8-trimethylandrost-1-en-3-one*; **4**). Colorless prisms. $[\alpha]_D^{16} = +15.8$ ($c = 0.5$, $CHCl_3$). UV (MeCN): 231 (3.91), 218 (4.24). IR (KBr): 3433, 1744, 1655. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (pos.): 527 ($[M+H]^+$). HR-ESI-MS: 527.2647 ($[M+H]^+$, $C_{30}H_{39}O_8^+$; calc. 527.2645).

Toonaciliatone F (=*6α,7α-Diacetoxy-21,23-epoxy-24,25,26,27-tetranorapotirucalla-1,20,22-triene-3,15-dione*; *(5α,6α,7α,13α,17α)-6,7-Bis(acetyloxy)-17-(furan-3-yl)-4,4,8-trimethylandrost-1-ene-3,15-dione*; **5**). White powder. $[\alpha]_D^{21} = +13.6$ ($c = 0.3$, $CHCl_3$). UV (MeCN): 231 (3.93), 218 (4.23). IR (KBr): 1754, 1731, 1668. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (pos.): 511 ($[M+H]^+$). HR-ESI-MS: 511.2704 ($[M+H]^+$, $C_{30}H_{39}O_7^+$; calc. 511.2696).

REFERENCES

[1] D. E. Champagne, O. Koul, M. B. Isman, G. G. E. Scudder, G. H. N. Towers, *Phytochemistry* **1992**, *31*, 377; A. Roy, S. Saraf, *Biol. Pharm. Bull.* **2006**, *29*, 191; D. A. Mulholland, B. Parel, P. H. Coombes, *Curr. Org. Chem.* **2000**, *4*, 1011.

[2] S. K. Chen, B. Y. Chen, H. Li, in 'Flora Reipublicae Popularis Sinicae (Zhongguo Zhiwu Zhi)', Science Press, Beijing, 1997, Vol. 43, pp. 239–240.

[3] The Editorial Committee of the Administration Bureau of Traditional Chinese Medicine, 'Chinese Materia Medica (Zhonghua Benchao)', Shanghai Science and Technology, Shanghai, 1999, Vol. 5, pp. 44–45.

[4] a) S. M. Agostinho, M. F. Das, G. F. Da Silva, J. B. Fernandes, P. C. Vieira, A. L. Pinheiro, E. F. Vilela, *Biochem. Syst. Ecol.* **1994**, *22*, 323; b) J. O. Neto, S. M. M. Agostinho, M. F. Das G. F. Da Silva, P. C. Vieira, J. B. Fernandes, A. L. Pinheiro, E. F. Vilela, *Phytochemistry* **1995**, *38*, 397.

[5] J. Q. Neto, M. F. das G. F. da Silva, J. B. Fernandes, P. C. Vieira, A. L. Pinheiro, *Phytochemistry* **1998**, *49*, 1369; S.-G. Liao, S.-P. Yang, T. Yuan, C.-R. Zhang, H.-D. Chen, Y. Wu, Y.-K. Xu, J.-M. Yue, *J. Nat. Prod.* **2007**, *70*, 1268.

[6] R. Chowdhury, *Biochem. Syst. Ecol.* **2004**, *32*, 103; T. A. M. Veiga, R. González-Vázquez, J. O. Neto, M. F. G. F. Silva, B. King-Díaz, B. Lotina-Hennsen, *Arch. Biochem. Biophys.* **2007**, *465*, 38.

[7] A. Chatterjee, T. Chakrabortty, S. Chandrasekharan, *Phytochemistry* **1971**, *10*, 2533.

[8] I. G. Grant, J. A. Hamilton, T. A. Hamor, R. Hodges, S. G. McGeachin, R. A. Raphael, J. M. Robertson, G. A. Sim, *Proc. Chem. Soc.* **1961**, 444; G. W. Gopinath, T. R. Govidachari, P. C. Parthasarathy, N. Wiswanathan, D. Arigoni, W. C. Wildman, *Proc. Chem. Soc.* **1961**, 446.

[9] S. Singh, H. S. Garg, N. M. Khanna, *Phytochemistry* **1976**, *15*, 2001.

[10] T. Cairns, G. Eglinton, S. G. Mc Geachin, *J. Chem. Soc.* **1965**, 1235.

[11] J. Ning, H.-P. He, S.-F. Li, Z.-L. Geng, X. Fang, Y.-T. Di, S.-L. Li, X.-J. Hao, *J. Asian Nat. Prod. Res.* **2010**, *12*, 448.

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