Tricycloalternarenes A – E: Five New Mixed Terpenoids from the Endophytic Fungal Strain *Alternaria alternata* Ly83

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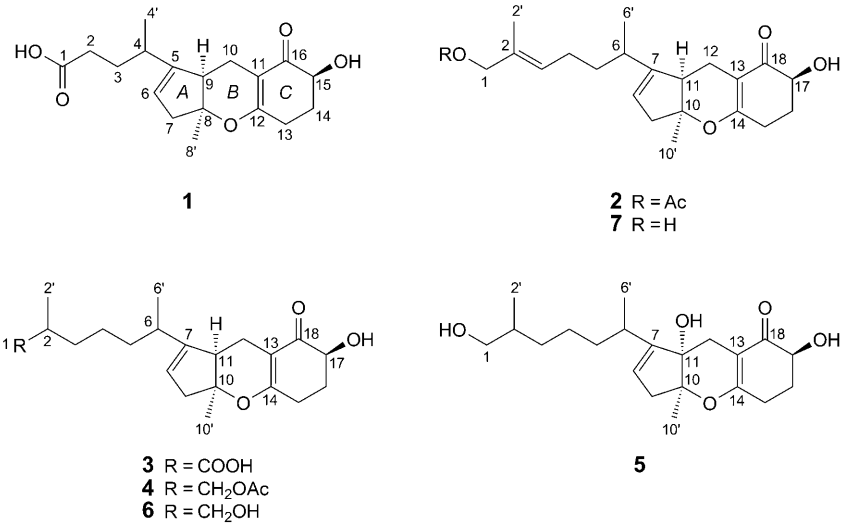
Five new mixed terpenoids, tricycloalternarenes (TCAs) A – E (**1** – **5**), together with two known compounds, TCA 1b (**6**) and TCA 2b (**7**), were isolated from the solid-state-cultured endophytic fungus *Alternaria alternata* of *Maytenus hookeri*. Their structures were identified by extensive spectroscopic (especially 2D-NMR) experiments. Compound **7** showed weak activity against human tumor cell lines by MTT assay.

Introduction. – *Alternaria alternata* and its pathotypes are widely distributed in plants, foods, and indoor air environment. They not only can cause brown spot disease of mandarins, tobacco, or other plants [1][2], but also are involved in postharvest diseases of fruits and grains [3 – 5]. Previous chemical studies established the occurrence of cyclic peptides, polyketides and mixed terpenoids from this genus, some of them being bioactive [6 – 10]. Particularly, the backbone of the mixed terpenoids are characterized with the combination of three isoprene units biosynthesized *via* the classic mevalonate pathway and a nonterpenoid part, a six-membered cyclic α,β-unsaturated ketone [11].

During our researches on plant endophytes, *A. alternata* was isolated as one of endophytic fungi of *Maytenus hookeri*. In order to study the interactions between *A. alternata* and its host plant *M. hookeri*, *A. alternata* was incubated on *Murashige – Skoog* (MS) agar [12], the plant culture medium. Five new mixed terpenoids, TCAs A – E (**1** – **5**), together with two known TCAs (tricycloalternarenes, named by *Liebermann et al.*) [8], TCA 1b (**6**) and TCA 2b (= ACTG-toxin D) (**7**) [8][13], were found. In this work, we report their isolation and structure elucidation.

Results and Discussion. – TCA A (**1**) was obtained as a colorless oil. HR-ESI-MS analysis of **1** showed a quasimolecular ion peak at *m/z* 321.1693 ($[M+H]^+$; calc. 321.1701), corresponding to the molecular formula $C_{18}H_{24}O_5$. The IR spectrum indicated the presence of OH groups (3392 cm^{-1}) and a CO group (1707 cm^{-1}). The ^{13}C-NMR spectrum exhibited signals for 18 C-atoms, including six quaternary ones, four CH groups, six CH_2 groups and two Me groups. Comparison of the ^{1}H- and ^{13}C-NMR spectroscopic data of **1** (*Tables 1* and *2*) with those of the known compound TCA 2b (**7**) [8][13], which was also isolated in this study, revealed that **1** had the same tricyclic moiety as **7**, but not the same side chain. Signals for a C=C bond, a Me group



and a CH_2OH group as in the side chain of **7** were absent, but a quaternary C-atom at δ(C) 178.5 appeared in **1**, indicating the presence of a CO group at the end of the side chain of **1**, which was confirmed by the HMBC correlations from H–C(2) and H–C(3) to C(1) (δ(C) 178.5). Furthermore, correlations of Me(4′) (δ(C) 20.1) with C(3) (δ(C) 29.3) and C(5) (δ(C) 148.8) were observed in the HMBC spectrum. In combination with ^{1}H,^{1}H-COSY and ^{1}H,^{1}H-TOCSY correlations of H–C(2)/H–C(3)/H–C(4) and Me(4′)/H–C(4), the side chain was connected to the tricyclic moiety at C(5) in ring *A* (*Fig.*).

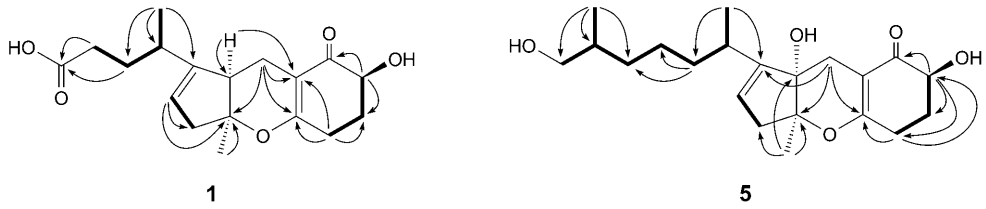


Figure. *Key COSY* (—) *and HMBC* (→) *correlations for* **1** *and* **5**

The relative configuration of **1** was determined based on ROESY experiments. The correlation between Me(8′) and H–C(9) revealed that the *A* and the *B* ring in **1** were *cis*-fused, which was similar with those of TCA 1b (**6**) and TCA 2b (**7**), whose stereochemistry had been determined by X-ray crystallography [13]. In addition, a modified *Mosher* method was applied to determine the absolute configuration of C(15) [14]. After the treatment with (trimethylsilyl)diazomethane ($TMSCHN_2$) [15], the methyl ester of **1** was obtained, and subsequently transformed into the (*S*)-MTPA

Table 1. *^{1}H-NMR Data of* **1**–**5**. At 400 MHz; δ in ppm, J in Hz.

	1[a])	**2**[a])	**3**[a])	**4**[a])	**5**[a])	**5**[b])
H–C(1)	–	4.43 (br. *s*)	–	3.89–3.92 (*m*), 3.80–3.83 (*m*)	3.36–3.43 (*m*)	3.16–3.20 (*m*), 3.06–3.09 (*m*)
H–C(2)	2.19–2.22 (*m*)	–	2.39–2.43 (*m*)	1.97–2.01 (*m*), 1.67–1.74 (*m*)	1.46–1.53 (*m*)	1.32–1.37 (*m*)
Me(2′)	–	1.61 (*s*)	1.14 (*d*, *J* = 5.5)	0.88 (*d*, *J* = 6.8)	0.87 (*d*, *J* = 6.4)	0.73 (*d*, *J* = 6.6)
H–C(3)	1.73–1.81 (*m*), 1.61–1.64 (*m*)	5.41 (*t*, *J* = 7.0)	1.57–1.62 (*m*), 1.36–1.39 (*m*)	1.25–1.32 (*m*), 1.04–1.11 (*m*)	1.25–1.31 (*m*), 0.94–1.01 (*m*)	1.20–1.24 (*m*), 0.81–0.86 (*m*)
H–C(4)	2.02–2.05 (*m*)	1.92–1.96 (*m*)	1.20–1.25 (*m*)	1.20–1.27 (*m*)	1.23–1.28 (*m*), 1.13–1.17 (*m*)	1.07–1.11 (*m*)
Me(4′)	0.95 (*d*, *J* = 5.21)	–	–	–	–	–
H–C(5)	–	1.47–1.52 (*m*), 1.31–1.37 (*m*)	1.41–1.44 (overlapped), 1.23–1.27 (*m*)	1.41–1.45 (overlapped), 1.20–1.25 (*m*)	1.32–1.36 (*m*), 1.14–1.20 (*m*)	1.27–1.32 (overlapped), 1.04–1.08 (*m*)
H–C(6)	5.33 (br. *s*)	2.00–2.03 (*m*)	1.97–2.02 (*m*)	1.97–2.02 (*m*)	2.10–2.15 (*m*)	2.00–2.03 (*m*)
Me(6′)	–	0.97 (*d*, *J* = 6.8)	0.95 (*d*, *J* = 5.6)	0.95 (*d*, *J* = 6.8)	1.10 (*d*, *J* = 6.8)	1.01 (*d*, *J* = 6.8)
H_α–C(7)	2.56 (*d*, *J* = 16.1)	–	–	–	–	–
H_β–C(7)	2.39 (*d*, *J* = 16.4)	–	–	–	–	–
H–C(8)	–	5.32 (br. *s*)	5.30 (br. *s*)	5.30 (br. *s*)	5.58 (br. *s*)	5.43 (br. *s*)
Me(8′)	1.41 (*s*, 3 H)	–	–	–	–	–
H_α–C(9)	–	2.61 (*d*, *J* = 16.2)	2.59 (*d*, *J* = 16.1)	2.60 (*d*, *J* = 16.0)	2.54 (*dd*, *J* = 2.6, 16.8)	2.33 (*d*, *J* = 16.0)
H_β–C(9)	2.75 (br. *s*)	2.45 (*d*, *J* = 16.2)	2.39–2.43 (*m*)	2.39–2.43 (*m*)	2.64 (*d*, *J* = 16.8)	2.57 (*d*, *J* = 16.0)
H_α–C(10)	2.68 (*d*, *J* = 16.8)	–	–	–	–	–
H_β–C(10)	2.13–2.17 (*m*)	–	–	–	–	–
Me(10′)	–	1.43 (*s*)	1.41 (*s*)	1.42 (*s*)	1.42 (*s*)	1.27 (*s*)
H–C(11)	–	2.74 (br. *s*)	2.71 (br. *s*)	2.72 (br. *s*)	–	–
H_α–C(12)	–	2.68 (*d*, *J* = 17.0)	2.64 (*d*, *J* = 16.9)	2.67 (*d*, *J* = 17.0)	2.96 (*d*, *J* = 16.8)	2.64 (*d*, *J* = 15.3)
H_β–C(12)	–	2.20–2.25 (*m*)	2.20–2.25 (*m*)	2.20–2.24 (*m*)	2.20 (*dd*, *J* = 2.4, 16.8)	1.98 (*d*, *J* = 16.6)
H_α–C(13)	2.34–2.39 (*m*)	–	–	–	–	–
H_β–C(13)	2.42–2.49 (*m*)	–	–	–	–	–
H_α–C(14)	1.73–1.81 (*m*)	–	–	–	–	–
H_β–C(14)	2.23–2.26 (*m*)	–	–	–	–	–
H_α–C(15)	–	2.35–2.38 (*m*)	2.37–2.41 (*m*)	2.38–2.41 (*m*)	2.30–2.36 (*m*)	2.16 (*d*, *J* = 16.4)
H_β–C(15)	4.05 (*dd*, *J* = 4.2, 10.2)	2.45–2.51 (*m*)	2.44–2.50 (*m*)	2.45–2.52 (*m*)	2.46–2.52 (*m*)	2.43–2.48 (overlapped))
H_α–C(16)	–	1.68–1.73 (*m*)	1.72–1.78 (*m*)	1.66–1.74 (*m*)	1.66–1.71 (*m*)	1.47–1.53 (*m*)
H_β–C(16)	–	2.30–2.35 (*m*)	2.29–2.36 (*m*)	2.31–2.36 (*m*)	2.30–2.35 (*m*)	2.01–2.03 (*m*)
H–C(17)	–	4.04 (*dd*, *J* = 5.2, 12.8)	4.06 (*dd*, *J* = 4.1, 10.3)	4.03 (*dd*, *J* = 5.0, 12.6)	4.07 (*dd*, *J* = 5.4, 13.0)	3.85–3.90 (*m*)
MeCO	–	2.07 (*s*)	–	2.05 (*s*)	–	–

[a]) Measured in $CDCl_3$. [b]) Measured in (D_6)DMSO.

(MTPA = α-methoxy-α-(trifluoromethyl)phenylacetyl chloride) and (*R*)-MTPA esters by the procedure described in the *Exper. Part*. On the basis of the values of $\Delta\delta$ ($\delta(S) - \delta(R)$), the absolute configuration of C(15) was determined to be (*S*). Therefore, compound **1** was elucidated as 4-[(3a*S*,7*S*,9a*R*)-3,3a,5,6,7,8,9,9a-octahydro-7-hydroxy-3a-methyl-8-oxocyclopenta[*b*]chromen-1-yl]pentanoic acid.

Table 2. *^{13}C-NMR Data of* **1**–**5**. At 100 MHz; δ in ppm.

	1[a])	**2**[a])	**3**[a])	**4**[a])	**5**[a])	**5**[b])
C(1)	178.5 (*s*)	70.2 (*t*)	180.9 (*s*)	69.4 (*t*)	68.7 (*t*)	66.2 (*t*)
C(2)	31.8 (*t*)	129.9 (*s*)	38.9 (*d*)	32.3 (*d*)	35.3 (*d*)	35.2 (*d*)
C(2′)	–	13.9 (*q*)	16.8 (*q*)	16.8 (*q*)	16.5 (*q*)	16.7 (*q*)
C(3)	29.3 (*t*)	129.5 (*d*)	33.6 (*t*)	33.4 (*t*)	33.0 (*t*)	33.0 (*t*)
C(4)	31.7 (*d*)	25.7 (*t*)	24.8 (*t*)	24.6 (*t*)	24.6 (*t*)	23.9 (*t*)
C(4′)	20.1 (*q*)	–	–	–	–	–
C(5)	148.8 (*s*)	34.3 (*t*)	34.6 (*t*)	34.8 (*t*)	36.3 (*t*)	35.8 (*t*)
C(6)	120.5 (*d*)	32.4 (*d*)	32.5 (*d*)	32.7 (*d*)	31.1 (*d*)	30.6 (*d*)
C(6′)	–	20.1 (*q*)	20.2 (*q*)	20.1 (*q*)	21.3 (*q*)	21.2 (*q*)
C(7)	44.9 (*t*)	149.9 (*s*)	150.2 (*s*)	150.2 (*s*)	153.2 (*s*)	152.0 (*s*)
C(8)	88.4 (*s*)	120.0 (*d*)	119.8 (*d*)	119.8 (*d*)	125.1 (*d*)	123.3 (*d*)
C(8′)	23.1 (*q*)	–	–	–	–	–
C(9)	46.1 (*d*)	44.8 (*t*)	44.9 (*t*)	44.8 (*t*)	42.5 (*t*)	42.3 (*t*)
C(10)	14.8 (*t*)	88.3 (*s*)	88.3 (*s*)	88.3 (*s*)	89.7 (*s*)	89.3 (*s*)
C(10′)	–	23.3 (*q*)	23.4 (*q*)	23.3 (*q*)	18.2 (*q*)	18.4 (*q*)
C(11)	104.9 (*s*)	46.1 (*d*)	46.3 (*d*)	46.2 (*d*)	81.1 (*s*)	79.4 (*s*)
C(12)	172.6 (*s*)	15.2 (*t*)	15.5 (*t*)	15.3 (*t*)	22.6 (*t*)	23.1 (*t*)
C(13)	27.7 (*t*)	105.0 (*s*)	105.2 (*s*)	105.1 (*s*)	104.6 (*s*)	104.7 (*s*)
C(14)	29.2 (*t*)	172.3 (*s*)	172.5 (*s*)	172.3 (*s*)	171.3 (*s*)	169.4 (*s*)
C(15)	70.9 (*d*)	27.7 (*t*)	27.7 (*t*)	27.7 (*t*)	27.3 (*t*)	26.8 (*t*)
C(16)	197.9 (*s*)	29.4 (*t*)	29.5 (*t*)	29.4 (*t*)	29.3 (*t*)	29.5 (*t*)
C(17)	–	70.9 (*d*)	71.0 (*d*)	70.9 (*d*)	70.9 (*d*)	70.1 (*d*)
C(18)	–	197.7 (*s*)	197.8 (*s*)	197.7 (*s*)	197.3 (*s*)	196.8 (*s*)
Me*C*O	–	171.0 (*s*)	–	171.3 (*s*)	–	–
*Me*CO	–	21.0 (*q*)	–	20.9 (*q*)	–	–

[a]) Measured in $CDCl_3$. [b]) Measured in (D_6)DMSO.

TCA B (**2**) was obtained as a colorless powder. The molecular formula of **2** was $C_{23}H_{32}O_5$, as ascertained by positive-ion HR-ESI-MS ($[M+H]^+$ at *m/z* 389.2332; calc. 389.2327). The ^{1}H- and ^{13}C-NMR spectra of **2** (*Tables 1* and *2*) closely resembled those of TCA 2b (**7**); the only difference between **2** and **7** was that the former had one more acetyl group than the latter, which was readily located to be at the OH group at C(1) (δ(C) 70.2) by the HMBC correlations from H–C(1) (δ(H) 4.43, br. *s*) to the Ac CO C-atom (δ(C) 171.0). The ROESY correlation between H–C(1) and H–C(3) (δ(H) 5.41, *t*, *J* = 7.0) indicated the geometry of the C(2)/C(3) C=C bond to be (*E*).

TCA C (**3**) was obtained as a colorless oil with the molecular formula $C_{21}H_{30}O_5$ based on HR-ESI-MS ($[M+H]^+$ at *m/z* 363.2167; calc. 363.2171). Compound **3** exhibited very similar physical and spectroscopic data to those of TCA 1b (**6**) [8][13], which was also isolated in this study, except that $HOCH_2$ at C(1) in **6** was oxygenated to COOH (δ(C) 180.9) in **3**. This difference was verified by the HMBC correlations from H–C(2), H–C(3) and Me(2′) to C(1) (δ(C) 180.9), respectively.

TCA D (**4**) was isolated as a colorless powder. Compound **4** had a quasimolecular ion peak at *m/z* 391.2492 ($[M+H]^+$; calc. 391.2484) in the positive-ion HR-ESI-MS, which determined the molecular formula to be $C_{23}H_{34}O_5$. In comparison with TCA 1b (**6**), the ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) of **4** presented one more AcO group

than **6**, corresponding to the HMBC correlation from MeCO (δ(H) 2.05, *s*) to CO (δ(C) 171.3). The HMBC correlation from H–C(2) to the Ac CO C-atom conformed the AcO substitution at C(1).

TCA E (**5**) was isolated as a colorless powder and established to have the molecular formula $C_{21}H_{32}O_5$ by HR-ESI-MS ($[M+H]^+$, at *m*/*z* 365.2325; calc. 365.2327). The ^{1}H- and ^{13}C-NMR spectra of **5** (*Tables 1* and *2*) were similar to those of TCA 1b (**6**), and the only difference was the replacement of the CH C-atom signal at C(11) (δ(C) 46.3) in **6** by a quaternary C-atom signal (δ(C) 81.1) in **5**, revealing OH substitution at C(11), which was confirmed by HMBC correlations from H_α–C(9), Me(10′) (δ(H) 1.42, *s*) and H–C(12) to C(11) (*Fig.*). When the solvent for the NMR experiment of **5** was changed from $CDCl_3$ to (D_6)DMSO, three OH signals, including HO–C(1) (δ(H) 4.31, *t*, $J = 5.2$), HO–C(11) (δ(H) 4.73, *s*), and HO–C(17) (δ(H) 4.90, *d*, $J = 3.2$), were observed. The ROESY correlation between the OH H-atom at C(11) and Me(10′) indicated α-position for OH and *cis*-form of the *A*/*B* cyclic system.

Known TCAs have been reported to act as non-specific toxins and show positive results in leaf-puncture assays by causing spreading brown lesions and necrotic effects [8][10][13]. In order to study their cytotoxic activities, we screened some TCAs for antitumor activity, using the SRB (sulforhodamine B) method [16]. The major metabolite, compound **7**, showed 88.6% and 98.7% inhibition against tumor cell lines A-549 and HL-60 at 16 μg/ml, respectively.

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Experimental Part

General. Trimethylsilyldiazomethane ($TMSCHN_2$) was from *Aldrich*. (+)-(*R*), and (–)-(*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA) were from *Alfa Aesar*. Column chromatography (CC) was performed on silica gel *H* (SiO_2, 200–300 mesh or 10–40 μm, *Qingdao Marine Chemical Factory*, China), *Sephadex LH-20* gel (*Amersham Pharmacia*, Sweden) and *RP-18* (reverse-phase C_{18}) SiO_2 (40–63 μm, *Merck*, Germany). TLC was performed on SiO_2 GF_{254} (10–40 μm; *Qingdao*). Prep. TLC (1.0–1.5 mm) was conducted with precoated silica gel GF_{254} (10–40 μm; *Qingdao*) glass plates (10×20 or 20×20 cm), and spots were visualized under UV light. Optical rotations: *Jasco DIP-370* digital polarimeter. UV Spectra: *Shimadzu 2401PC* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bio-Rad FTS-135* spectrophotometer with KBr discs; in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AM-400* and *DRX-500* instruments, resp.; chemical shifts δ in ppm rel. to Me_4Si, coupling constants *J* in Hz. ESI-MS and HR-ESI-MS: *Finnigan LCQ-Advantage* and *VG Auto-Spec-3000* mass spectrometers, resp.; in *m*/*z*.

Microbial Material. The fungal strain Ly83 of *A. alternata* was isolated from the leaves of *M. hookeri* collected from Xishuangbanna Tropical Plant Garden, Chinese Academy of Sciences, Yunnan Province, P. R. China. Surface-sterilized samples were cut into 1 cm fragments, and ten fragments from each sample, taken from different regions of the leaves, were placed on 1.5% potato-dextrose-agar (PDA). The plates were incubated at 28° for more than 7 d. Hyphal tips of the developing fungal colonies were transferred onto fresh PDA plates. After purifying the isolates several times, the final pure cultures were transferred to PDA slants. The isolated fungus was identified to be *Alternaria alternata* (Fr.: Fr.) KEISSLER. The fungal strain was stored in 20% glycerol, and seed cultures were started from cultures

incubated on PDA slants at 28° for 5 d. Solid-state fermentation was carried out on MS agar (5 l; pH = 5.8) supplemented with NAA (α-naphthaleneacetic acid, 2.0 mg/l), kinetin (6-furfurylaminopurine, 0.1 mg/l), and agar (13 g/l), and the cultures were incubated at 28° for 10 d.

Extraction and Isolation. Agar from the culture of *A. alternata* Ly83 was chopped, diced, and extracted with AcOEt/MeOH/AcOH (80:15:5) (3×). The removal of solvents under vacuum produced the crude extracts which were partitioned between H_2O and AcOEt (5×). The org. layers were collected. After the removal of solvents under vacuum, extracts (2.74 g) were obtained. The AcOEt extracts were subjected to medium pressure liquid chromatography over *RP-18* SiO_2 (145 g), eluted with H_2O, 30%, 50%, 70%, and 100% Me_2CO (2 l for each gradient) to yield 5 fractions, *Fr. 1–5*. For every solvent system, one fraction was collected. *Fr. 2* (242 mg) was divided into seven subfractions (*Fr. 2.1–Fr. 2.7*) by CC over SiO_2 *H* (200–300 mesh) using a petroleum ether (PE)/Me_2CO gradient. Further separations by repeated SiO_2 *H* (10–40 μm) CC, prep. TLC developed with $CHCl_3$/MeOH/HCO_2H or H_2O-saturated AcOEt, and CC over *Sephadex LH-20* eluted with Me_2CO yielded TCA A (**1**) (5 mg) and TCA E (**5**) (4 mg). TCA C (**3**) (4 mg), TCA 1b (**6**) (2 mg), and TCA 2b (**7**) (15 mg) were obtained from *Fr. 3* (450 mg) by repeated CC over SiO_2 *H* (200–300 mesh or 10–40 μm) and prep. TLC developed with $CHCl_3$/MeOH/HCO_2H or PE/$CHCl_3$/MeOH, followed by purification with CC over *Sephadex LH-20* eluted with Me_2CO. *Fr. 4* (230 mg) was subjected to prep. TLC developed with PE/Me_2CO (8:2) to afford seven subfractions (*Fr. 4.1–Fr. 4.7*). Furthermore, TCA B (**2**) (2 mg) and TCA D (**4**) (2 mg) were isolated by CC over SiO_2 *H* (10–40 μm) and CC over *Sephadex LH-20* eluted with Me_2CO from *Fr. 4.4* and *Fr. 4.3*, resp.

Preparation of Mosher *Esters.* The methyl ester by reaction with $TMSCHN_2$ was prepared from **1** by a procedure published in the literature [15]. To a soln. of methyl ester of **1** (3 mg) in anh. pyridine (0.25 ml) was added either (*S*)- or (*R*)-MTPA-Cl (5 μl). The mixture was stirred at 30° for 12 h, evaporated, and purified by CC (*Sephadex LH-20* in acetone).

TCA A (=*4-[(3a*S*,7*S*,9a*R*)-3,3a,5,6,7,8,9,9a-Octahydro-7-hydroxy-3a-methyl-8-oxocyclopenta[*b*]-chromen-1-yl]pentanoic Acid*; **1**). Colorless oil. $[\alpha]_D^{25} = +150.2$ ($c = 0.48$, $CHCl_3$). UV ($CHCl_3$): 264 (4.13). IR (KBr): 3392, 2968, 2931, 1707, 1601, 1083. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 321.1693 ($[M+H]^+$, $C_{18}H_{25}O_5^+$; calc. 321.1701).

TCA B (=*(2*E*)-2-Methyl-6-[(3a*S*,7*S*,9a*R*)-3,3a,5,6,7,8,9,9a-octahydro-7-hydroxy-3a-methyl-8-oxocyclopenta[*b*]chromen-1-yl]hept-2-en-1-yl Acetate*; **2**). Colorless powder. $[\alpha]_D^{25} = +134.0$ ($c = 0.54$, $CHCl_3$). UV ($CHCl_3$): 263 (4.04). IR (KBr): 3432, 2925, 2854, 1734, 1620, 1075. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 389.2332 ($[M+H]^+$, $C_{23}H_{33}O_5^+$; calc. 389.2327).

TCA C (=*2-Methyl-6-[(3a*S*,7*S*,9a*R*)-3,3a,5,6,7,8,9,9a-octahydro-7-hydroxy-3a-methyl-8-oxocyclopenta[*b*]chromen-1-yl]heptanoic Acid*; **3**). Colorless oil. $[\alpha]_D^{25} = +94.1$ ($c = 0.25$, $CHCl_3$). UV ($CHCl_3$): 264 (4.06). IR (KBr): 3431, 2927, 2856, 1708, 1615, 1079. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 363.2167 ($[M+H]^+$, $C_{21}H_{31}O_5^+$; calc. 363.2171).

TCA D (=*2-Methyl-6-[(3a*S*,7*S*,9a*R*)-3,3a,5,6,7,8,9,9a-octahydro-7-hydroxy-3a-methyl-8-oxocyclopenta[*b*]chromen-1-yl]heptyl Acetate*; **4**). Colorless powder. $[\alpha]_D^{25} = +118.8$ ($c = 0.55$, $CHCl_3$). UV ($CHCl_3$): 262 (3.96). IR (KBr): 3440, 2926, 2854, 1737, 1619, 1076. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. HR-ESI-MS (pos.): 391.2492 ($[M+H]^+$, $C_{23}H_{35}O_5^+$; calc. 391.2484).

TCA E (=*(3a*S*,7*S*,9a*S*)-3a,5,6,7,9,9a-Hexahydro-7,9a-dihydroxy-1-(7-hydroxy-6-methylheptan-2-yl)-3a-methylcyclopenta[*b*]chromen-8(3*H*)-one*; **5**). Colorless powder. $[\alpha]_D^{30} = +155.2$ ($c = 0.66$, $CHCl_3$). UV ($CHCl_3$): 264 (4.06). IR (KBr): 3431, 2925, 2854, 1618, 1074, 1042. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS (pos.): 365.2325 ($[M+H]^+$, $C_{21}H_{33}O_5^+$; calc. 365.2327).

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