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Tetranortriterpenoid derivatives from *Turraea parvifolia* (Meliaceae)

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Abstract

The methanol extract of the seeds of *Turraea parvifolia* has yielded seven novel triterpenoid derivatives: 12α-acetoxyazadironolide, turraparvin A (12α-acetoxy-7α,23-dihydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-21,23-olide), turraparvin B (12α-acetoxy-7α,21-dihydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-23,21-olide), turraparvin C (7α,12α-diacetoxy-21-hydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-23,21-olide), 11-*epi*-21-hydroxytoonacilide, 11-*epi*-23-hydroxytoonacilide and turraparvin D (12α-acetoxy-7α-hydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-21,23-lactam).

Keywords: Meliaceae; *Turraea parvifolia*; 12α-Acetoxyazadironolide; Turraparvin A; Turraparvin B; Turraparvin C; 11-*epi*-21-Hydroxytoonacilide, 11-*epi*-23-Hydroxytoonacilide and turraparvin D

1. Introduction

Turraea parvifolia Defl. (Meliaceae) is a small tree or shrub found in East Africa. It is usually found in open *Acacia-Commiphora* bush-land, especially around rock outcrops and on banks of seasonal watercourses. It is characterized by its smooth, dark grey stems, slender drooping branches and small white flowers (Blundell, 1987). It is known as "Chositim" by the Pokot tribe of Kenya, where it is used as an emetic.

The genus *Turraea* (Meliaceae) is placed in the tribe Turraeae, subfamily Meliodeae (Styles and White, 1991). The genus comprises some 60–70 species of shrubs and small trees widely distributed in eastern Africa and the islands of the Indian Ocean. *Turraea* species are widespread, but they are nowhere common, or at least are inconspicuous and, therefore, difficult to obtain (Bentley et al., 1995; Mulholland and Taylor, 1988). Seven species of the genus *Turraea* have been investigated chemically and a number of limonoids, protolimonoids and triterpenoids have been isolated (Adul et al., 1993; Akinniyi et al., 1986; Bentley et al., 1992, 1995; Chiplunkar et al., 1993; Fraser et al., 1994, 1995; Mulholland and Taylor, 1988; Mulholland et al., 1993, 1998, 1999; Rajab et al., 1988; Torto et al., 1995, 1996).

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2. Results and discussion

Six novel triterpenoid derivatives and one novel tetranortriterpenoid lactam were isolated from the methanol extract of the seed of *Turraea parvifolia*. As six of the compounds isolated were hydroxybutenolides and these occur as epimeric mixtures of the interconverting α- and β-hydroxy compounds in solution, NMR spectra were complex and some pairing of some peaks occurred (Kraus and Grimminger, 1980; Siddiqui et al., 1999). The peak due to the major epimer is given in the text, with that due to the minor one in brackets.

High resolution mass spectrometry of compound **1**, turraparvin A, showed no molecular ion peak, however, fragment ion peaks were observed at *m/z* 466.2367 [M^+-18], 424.2251 [M^+-60] and 406.2119 [M^+-18-60] due to the loss of water, acetic acid or both water and acetic acid. The molecular formula of $C_{28}H_{36}O_7$ was deduced from the mass spectrum in conjugation with the ^{13}C NMR spectrum. Rings A–D were intact, an α,β-unsaturated ketone in ring A was indicated by a pair of doublets at δ 7.01 (J = 10.2 Hz, H-1) and δ 5.81 (J = 10.2 Hz, H-2) and resonances at δ 157.45 (157.41), δ 125.60 and δ 204.98 (204.95) ascribed to C-1, C-2 and C-3 respectively. A Δ^{14}-double bond was indicated by resonances at δ 158.46 (158.80) and δ 121.75 (121.95) for C-14 and C-15 respectively, and a resonance ascribed to H-15 at δ 5.64.

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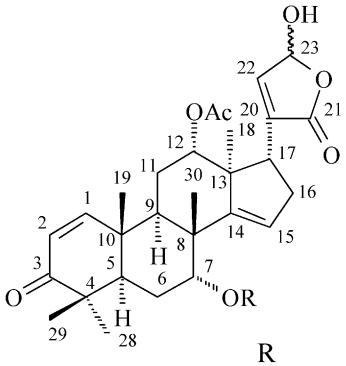
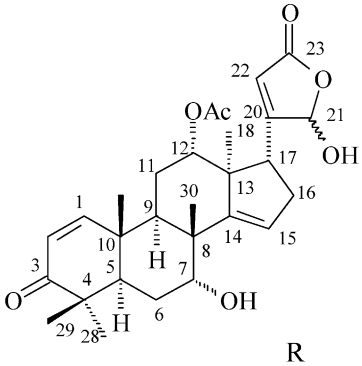
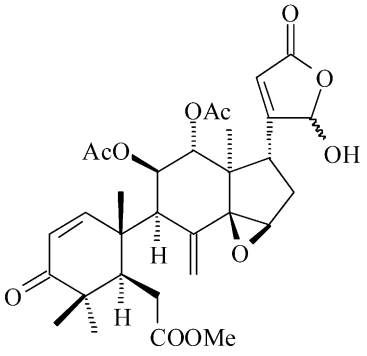


	R
(1)	H
(2)	Ac



	R
(3)	H
(4)	Ac



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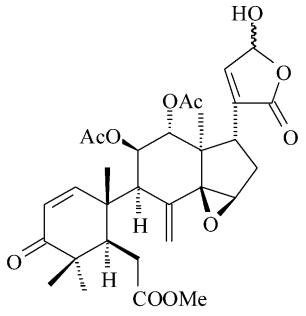

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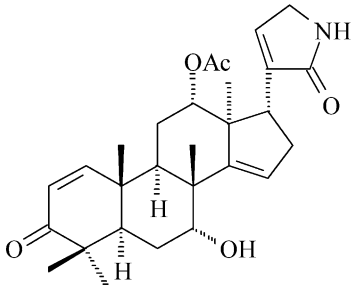

(7)

A hydroxy and an acetate group were present at C-7α and C-12α respectively. The H-7 resonance at δ 4.02 was assigned based on HMBC correlation with C-5 and a NOESY correlation with 3H-30, confirmed H-7 was β and thus, the hydroxy group was α. The H-12 resonance at δ 4.95 showed HMBC correlations with C-18 and C-17. The H-12 resonance showed a correlation with the 3H-30 resonance and the acetate methyl group proton resonance showed NOESY correlations with 3H-18 and H-9, confirming that the acetoxy group was in the α-orientation. The presence of a 23-hydroxy-21,23-butenolide side chain was indicated by a C-21 lactone carbonyl carbon resonance at δ 171.38 (171.33), a C-20,C-22 double bond indicated by resonances at δ 137.03 (137.94) and δ 144.92 (145.57). The H-22 (δ 6.95) resonance was seen to be coupled to H-23 in the COSY spectrum and C-23 occurred at δ 96.40 (96.12). The relative stereochemistry at C-5, C-9 and C-17 was confirmed for all compounds isolated by means of the NOESY spectrum. The H-9α resonance was seen to correlate with 3H-18 and 3H-28 (which are α) and H-5 also showed a correlation with the 3H-28 resonance. The H-17 resonance showed a NOESY correlation with H-12β confirming the β-orientation of H-17. All ^{1}H and ^{13}C NMR resonances could be assigned using COSY, HMBC and NOESY spectra and are given in Tables 1 and 2.

Compound **2** ($C_{30}H_{38}O_8$) was identified as 12α-acetoxyazadironolide, **2**. This compound is the 7-acetyl derivative of turraparvin A and this was confirmed by acetylation of turraparvin A which gave 12α-acetoxyazadironolide. This compound is a derivative of azadironolide previously isolated from *Azadirachta indica* (Siddiqui et al., 1999).

Compound **3** ($C_{28}H_{36}O_7$), turraparvin B, differed from **1** in the structure of the side-chain. Instead of a 23-hydroxy-21,23-butenolide ring, a 21-hydroxy-23,21-butenolide ring was present in **3**. This was confirmed by HMBC correlations Analogously, compound **4**, turraparvin C, ($C_{30}H_{38}O_8$) differs from compound **2** in having the 23-hydroxy-21,23-butenolide ring instead of the 21-hydroxy-23,21-butenolide ring.

The NMR spectra of compound **5**, 11-*epi*-21-hydroxytoonacilide, ($C_{31}H_{38}O_{11}$), showed that it was a ring B opened limonoid. Two H-30 resonances occurred as broad singlets at δ 5.34 and δ 5.27 and C-8 and C-30 occurred at δ 135.68 (135.49) and δ 122.29 (121.90) respectively. A carbomethoxy group was present at C-7 and the NMR spectrum showed C-7 occurring at δ 174.14 and the methoxy group proton resonance at δ 3.66 as is usual in ring-B opened limonoids (Kraus and Grimminger, 1980). An α,β-unsaturated ketone in ring A was indicated by a pair of doublets at δ 7.36 ($J = 10.6$, H-1) and δ 6.12 ($J = 10.6$, H-2) and resonances at δ 151.96 (152.07), δ 125.87 and δ 204.30 (204.19) ascribed to C-1, C-2 and C-3 respectively. No Δ^{14}-double bond was present, but a 14,15-epoxide was indicated by resonances at δ 71.30 (70.61) and δ 59.47 (58.97) and a resonance ascribed to H-15 at δ 3.92. The 14,15-epoxide was assigned a β-orientation due to a NOESY correlation between H-15 and H-30. Proton resonances ascribable to two acetoxy groups were present at δ 1.94 and δ 1.91 in the ^{1}H NMR spectrum. These were placed at C-11 and C-12 due to the presence of a H-9 (δ 2.96), H-11 (δ 5.54), H-12 (δ 5.65) coupled system seen in the

Table 1
NMR spectral data for compounds **1**–**7** (400 MHz, $CDCl_3$) (*J*, in Hz, given in parentheses)

^{1}H	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	7.01 *d* (10.2)	7.02 *d* (10.3)	7.01 *d* (10.3)	7.01 *d* (10.3)	7.36 *d* (10.6)	7.37 *d* (10.5)	7.00 *d* (10.2)
2	5.81 *d* (10.2)	5.81 *d* (10.1)	5.80 *d* (10.3)	5.84 *d* (10.3)	6.12 *d* (10.6)	6.16 *d* (10.5)	5.79 *d* (10.2)
3	–	–	–	–	–	–	–
4	–	–	–	–	–	–	–
5	2.37 *t* (5.1)	2.61 *m*	2.38 *m*	2.18 *m*	2.92 *m*	2.96 *m*	2.38 *m*
6	1.86 *m*	1.75 *m*	1.87 *m*	1.86 *m*	2.31 *m*	2.31 *m*	1.86 *m*
		1.95 *m*			2.45 *m*	2.45 *m*	
7	4.02 *bs*	5.26 *bs*	4.00 *bs*	5.26 *bs*	–	–	4.01 *bs*
8	–	–	–	–	–	–	–
9	2.43 *m*	2.39 *m*	2.39 *m*	2.36 *m*	2.96 *d* (6.6)	2.94 *d* (7.7)	2.38 *m*
10	–	–	–	–	–	–	–
11α	1.59 *dd* (7.5,9.2)	1.61 *m*	1.61 *m*	1.66 *m*	5.54 *dd* (6.6, 11.3)	5.51 *dd* (7.7, 10.3)	1.59 *dd* (14.2,6.8)
11β	2.42 *m*	2.51 *m*	2.44 *m*	2.46 *m*			2.55 *m*
12	4.95 *m*	4.93 *m*	4.96 *t* (8.0)	4.96 *m*	5.65 *d* (11.3)	5.66 *d* (10.3)	4.99 *m*
13	–	–	–	–	–	–	–
14	–	–	–	–	–	–	–
15	5.64 *bs*	5.43 *bs*	5.65 *d* (8.1)	5.49 *bs*	3.92 *s*	3.89 *s*	5.65 *bs*
16	2.58 *m*	2.49 *m*	2.57 *m*	2.47 *m*	1.85 *m*	2.10 *m*	2.48 *m*
					2.47 *m*	2.38 *m*	
17	3.00 *m*	2.92 *m*	2.98 *m*	2.94 *m*	2.99 *m*	2.99 *m*	3.05 *m*
18	1.01 *s*	1.01 *s*	1.03 *s*	1.02 *s*	0.95 *s*	0.97 *s*	1.00 *s*
19	1.16 *s*	1.19 *s*	1.15 *s*	1.18 *s*	0.96 *s*	0.94 *s*	1.16 *s*
20	–	–	–	–	–	–	–
21	–	–	6.04 *s*	6.05 *s*	5.81 *s*	–	–
22	6.95 *bs*	6.93 *bs*	5.97 *s*	5.95 *s*	5.88 *s*	6.84 *m*	6.87 *bs*
23	6.15 *bs*	6.14 *bs*	–	–	–	6.04 *m*	4.01 *bs*
28	1.14 *s*	1.04 *s*	1.13 *s*	1.19 *s*	1.06 *s*	0.97 *s*	1.14 *s*
29	1.06 *s*	1.04 *s*	1.05 *s*	1.05 *s*	1.07 *s*	1.07 *s*	1.06 *s*
30	1.16 *s*	1.21 *s*	1.15 *s*	1.21 *s*	5.34 *bs*	5.31 *bs*	1.15 *s*
					5.27 *bs*	5.22 *bs*	
Ac(CO)	–	–	–	–	–	–	–
Ac(CH_3)	1.92 *s*	1.97 *s*	2.11 *s*	2.13 *s*	1.94 *s*	1.89 *s*	1.89 *s*
Ac(CO)	–	–	–	–	–	–	–
Ac(CH_3)	–	1.95 *s*	–	1.97 *s*	1.91 *s*	1.85 *s*	–
OCH_3	–	–	–	–	3.66 *s*	3.66 *s*	–
NH	–	–	–	–	–	–	6.36 *bs*

COSY spectrum. The $J_{9,11}$ and $J_{11,12}$ coupling constants of 6.6 and 11.3 Hz respectively indicated that the acetate groups were at C-11β and C-12α (Mulholland et al., 1998). This was confirmed by NOESY correlations. The side-chain was found to be the 21-hydroxy-23,21-butenolide ring as in **3** and **4**. This was confirmed by HMBC correlations between C-17 and H-21, C-21 and H-22 and C-22 and both H-17β and H-21. Thus compound **5** was identified as 11-*epi*-21-hydroxytoonacilide. The 11-epimer, 21-hydroxytoonacilide has been isolated previously by Kraus and Grimminger (1980), and has been shown to exhibit feeding deterrents towards insects. The $J_{9,11}$ and $J_{11,12}$ coupling contants of 21-hydroxytoonacilide are both 4.1 Hz. (Kraus and Grimminger, 1980).

Compound **6,** $C_{31}H_{38}O_{11}$, was found to differ from **5** in having the 23-hydroxy-21,23-butenolide ring as in **1** and **2** and was identified as 11-*epi*-23-hydroxytoonacilide. The 11-epimer has been isolated by Kraus and Grimminger (1980), from *Toona ciliata* (Meliaceae).

Compound **7**, turraparvin D, was shown by HRMS to have a molecular formula $C_{28}H_{37}O_5N$. The tetracyclic structure of **7** was found to be the same as turraparvin A (**1**), with rings A–D intact, an α,β-unsaturated ketone in ring A indicated by a pair of doublets at δ 7.00 ($J = 10.2$, H-1) and δ 5.79 ($J = 10.2$, H-2) and resonances at δ 157.49, δ 125.54 and δ 204.88 ascribed to C-1, C-2 and C-3 respectively. A Δ^{14}-double bond was indicated by resonances at δ 158.73 and δ 122.16 and a resonance ascribed to H-15 at δ 5.65. An acetate group was present at C-12α and a hydroxy group at H-7α, with H-12β and H-7β occurring at δ 4.99 and δ 4.01 respectively. This left a side chain of molecular formula C_4H_4NO, suggesting the presence of a lactam. The C-21 carbonyl resonance occurred at δ 175.74. The C-20 and C-22 alkene carbon resonances occurred at δ 138.81 and δ 139.80 respectively and the methylene carbon, C-23, occurred at δ 46.52. The COSY spectrum showed coupling between H-22 (δ 6.87, bs) and the 2H-23 resonance at δ 4.01(bs) and assignments were supported by the HMBC and NOESY spectra. It was initially not possible to see resonances due to C-21 and C-20 in the ^{13}C NMR spectrum, but after lengthy re-running of the spectrum (120 h) and with the help of correlations seen in the HMBC spectrum, these peaks could be found. There has been one previous report of salannolactam-(21) a related lactam, by Kraus et al., from *Azadirachta indica* (Kraus et al., 1987). This lactam also co-occurred

Table 2
^{13}C NMR spectral data for compounds **1–7** (100 MHz, $CDCl_3$) (values in parentheses are due to the minor epimer)

Carbon	1	2	3	4	5	6	7
1	157.45 (157.41)	157.39	157.11	156.94	151.96 (152.07)	152.14 (152.00)	157.49
2	125.60	125.53	125.76 (125.79)	125.75	125.87	125.97 (125.88)	125.54
3	204.09	204.88	204.83	204.30	204.30 (204.19)	204.09	204.86
4	40.09	39.85	39.96	44.05	46.24	46.19	40.09
5	44.36	46.00	44.35	46.05	44.91	45.12	44.64
6	24.28	23.63	24.46	23.71	31.24	31.28	24.23
7	71.22 (71.21)	73.78	71.49 (71.26)	73.93 (73.77)	174.14	174.22	71.20
8	44.73	42.56	44.83	42.70	135.68 (135.49)	136.17	44.36
9	38.42 (38.44)	39.70	38.03	39.38	52.53 (52.65)	52.82	38.47
10	44.14	44.03	44.15	39.71	42.04	42.01	44.13
11	25.39	25.56	25.62	25.86	70.43 (71.15)	71.40	25.40
12	76.94 (76.91)	77.17	77.61	77.76	75.32 (75.71)	75.09 (75.02)	76.95
13	51.31 (51.47)	51.22 (51.35)	52.43 (52.39)	52.32	45.91	46.09 (45.83)	50.88
14	158.46 (158.80)	156.08 (156.38)	157.93	155.57	71.30 (70.61)	71.08	158.73
15	121.75 (121.95)	121.08 (120.91)	122.17 (121.75)	121.46	59.47 (58.97)	59.83 (59.52)	122.16
16	35.65 (35.35)	35.62	35.54 (35.91)	35.42	32.70 (32.30)	31.28 (29.84)	35.67
17	48.80 (48.62)	48.87	50.69 (51.15)	51.13 (50.77)	40.48 (40.18)	38.92 (38.19)	48.82
18	15.15 (15.23)	15.02 (15.08)	15.94	15.92	13.02	13.41 (13.45)	15.34
19	18.83	18.87 (18.85)	18.85	18.89 (18.99)	20.95	21.30	18.80
20	137.03 (136.94)	136.99	168.56 (167.48)	168.86	166.92 (167.29)	135.04 (135.64)	138.81
21	171.38 (171.33)	171.67	99.16 (99.55)	99.21 (99.63)	99.30 (99.37)	170.16 (170.73)	175.74
22	144.92 (145.57)	145.06 (145.74)	120.52 (118.26)	120.39 (121.23)	118.32 (120.35)	147.69 (146.57)	139.80
23	96.40 (96.12)	96.20 (96.58)	170.60 (170.72)	170.61	170.40	95.65 (96.08)	46.52
28	26.94	26.82	26.99	26.87	22.90 (22.87)	22.96	26.95
29	21.45	21.13	21.42	21.35	22.77	22.78	21.09
30	27.82 (27.86)	27.60	28.07	27.79 (27.65)	122.29 (121.90)	121.36	27.75
Ac(CO)	170.69 (170.72)	170.90	171.82	170.45	169.62	169.85	170.64
Ac(CO)	–	170.03	–	169.92	20.56	20.65	–
Ac(CH_3)	21.05	21.25	21.42	21.24	170.19 (171.55)	169.97	21.45
Ac(CH_3)	–	21.19	–	21.13	21.32	20.56	–
OCH_3	–	–	–	–	52.21	52.17	–

with compounds with hydroxybutenolide side-chains as in this case. The chemical shifts of C-20 to C-23 in salannolactam occurred at δ 140.9, δ 175.2, δ 138.0 and δ 46.8 and are in reasonably close agreement with chemical shifts for the same carbons in turraparvin D (δ 138 8, δ 175.7, δ 139.8 and δ 46.5).

3. Experimental

Seeds of *Turraea parvifolia* Defl. (Meliaceae) were collected from Chemolingot, Kenya identified by Mr. John Kisang and a voucher specimen retained (PC1) at Egerton University, Kenya. The ground seed (118.31 g) was left in methanol for 4 days. The methanol extract (9.27 g) yielded, after column chromatography over silica gel (Merck 9385) using 10% ethyl acetate in dichloromethane, turraparvin A (12α-acetoxy-7α,23-dihydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-21,23-olide), **1**, (12.2 mg), 12α-acetoxyazadironolide, **2**, (13.2 mg), turraparvin B (12α-acetoxy-7α,21-dihydroxy - 24,25,26,27 - tetranor - 3 - oxoapotirucalla - 1,14,20(22)-trien-23,21-olide), **3**, (8.9 mg), turraparvin C (7α,12α-diacetoxy-21-hydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-23,21-olide), **4**, (9.3 mg), 11-*epi*-21-hydroxytoonacilide, **5**, (10.3 mg), 11-*epi*-23-hydroxytoonacilide, **6**, (13.7 mg) and turraparvin D (12α-acetoxy-7α,hydroxy-24,25,26,27-tetranor-3-oxoapotirucalla-1,14,20(22)-trien-21,23-lactam), **7**, (5.4 mg). NMR data for compounds **1**–**7** is given in Tables 1 and 2.

IR spectra were recorded with a Nicolet Impact 400 D spectrometer on sodium chloride plates and calibrated against an air background. HRMS were obtained using a Kratos High Resolution MS 9/50 spectrometer at the Cape Technikon. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 MHz NMR spectrometer. Optical rotations were measured using a Perkin Elmer 241 Polarimeter with tube 10 cm in length. Melting points (uncorr.) were determined using a Köfler hot stage apparatus.

3.1. Turraparvin A (12.2 mg), 1

White crystalline; mp 108–110 °C; HRMS (rel. int.) *m/z*: at 466.2355 $[M–H_2O]^+$ ($C_{28}H_{34}O_6$ req. 466.2367, 2), 424.2251 $[M–CH_3COOH]^+$ (26), 406.2119 $[M–H_2O–CH_3COOH]^+$ (20), 391 (33), 373 (13), 345 (6), 295 (8), 269 (19), 239 (3), 211 (22), 150 (94), 109 (34), 71 (55) and 57 (100); IR: ν_{max}(NaCl) cm^{-1}: 3425, 2923, 2856, 1736, 1658 1462, 1250, 1038; $[\alpha]_D^{23}$ +36.8° ($CHCl_3$; *c* 0.20).

3.2. 12α-Acetoxyazadironolide (13.2 mg), 2

White crystalline; mp 97–99 °C; HRMS (rel. int.) *m/z*: 526.2560 $[M]^+$ ($C_{30}H_{38}O_8$ req. 526.2567, 1), 508.2510 $[M–H_2O]^+$ (1), 466.2366 $[M–CH_3COOH]^+$ (9), 406.2138 $[M–CH_3COOH–CH_3COOH]^+$ (14), 391 (15), 373 (7), 345 (3), 269 (14), 257 (28), 239 (31), 211 (17), 150 (100), 109 (17) and 69 (4); IR: ν_{max}(NaCl) cm^{-1}: 2971, 2860, 1732, 1474, 1393, 1252, 1135, 1034; $[\alpha]_D^{23}$ +63.1° ($CHCl_3$; *c* 0.20).

3.3. Turraparvin B (8.9 mg), 3

White crystalline; mp 142–144 °C; HRMS (rel. int.) *m/z*: 484.2449 $[M]^+$ ($C_{28}H_{36}O_7$ req. 484.2461, 3), 466.2346 $[M–H_2O]^+$ (24), 424.2240 $[M–CH_3COOH]^+$ (66), 388.2023 $[M–H_2O–H_2O–CH_3COOH]^+$ (21), 373 (15), 357 (36), 337 (18), 315 (12), 257 (19), 239 (33), 219 (66), 179 (78), 150 (60), 137 (99), and 109 (100); IR: ν_{max}(NaCl) cm^{-1}: 3420, 2926, 2859, 1742, 1670, 1465, 1254, 1115, 1042; $[\alpha]_D^{23}$ +29.1° ($CHCl_3$; *c* 0.09).

3.4. Turraparvin C (9.3 mg), 4

White crystalline; mp 117–119 °C; HRMS (rel. int.) *m/z*: 526.2573 $[M]^+$ ($C_{30}H_{38}O_8$ req. 526.2567, 5), 508.2492 $[M–H_2O]^+$ (20), 466.2361 $[M–CH_3COOH]^+$ (47), 406.2147 $[M–CH_3COOH–CH_3COOH]^+$ (44), 388.2030 $[M–H_2O–CH_3COOH–CH_3COOH]^+$ (42), 373 (20), 337 (13), 279 (14), 239 (60), 238 (37), 211 (19), 150 (80), 137 (90) and 57 (100); IR: ν_{max}(NaCl) cm^{-1}: 3388, 2915, 2849, 1741, 1670, 1389, 1246, 1130, 1042; $[\alpha]_D^{23}$ +35.2° ($CHCl_3$; *c* 0.14).

3.5. 11-epi-21-Hydroxytoonacilide (10.3 mg), 5

White crystalline; mp 124–126 °C; HRMS (rel. int.) *m/z*: 586.2416 $[M]^+$ ($C_{31}H_{38}O_{11}$ req. 586.2414, 97), 526.2204 $[M–CH_3COOH]^+$ (22), 508.2097 $[M–H_2O–CH_3COOH]^+$ (11), 466.1991 $[M–2\times CH_3COOH]^+$ (19), 484 (8), 467 (27), 449 (27), 391 (41), 297 (54), 281 (23), 239 (36), 210 (42), 149 (100), 105 (86) and 69 (61); IR: ν_{max}(NaCl) cm^{-1}: 2928, 2849, 1753, 1674, 1383, 1240, 1048; $[\alpha]_D^{23}$ +26.0° ($CHCl_3$; *c* 0.10).

3.6. 11-epi-23-Hydroxytoonacilide (13.7 mg), 6

White crystalline; mp 139–142 °C; HRMS (rel. int.) *m/z*: 586.2419 $[M]^+$ ($C_{31}H_{38}O_{11}$ req. 586.2414, 61), 568.2309 $[M–H_2O]^+$ (14), 526.2203 $[M–CH_3COOH]^+$ (14), 466.1991 $[M–2\times CH_3COOH]^+$ (24), 449 (25), 433 (20), 391 (54), 311 (43), 297 (100), 257 (25), 239 (46), 149 (84), 137 (57), 105 (68) and 57 (85); IR: ν_{max}(NaCl) cm^{-1}: 2929, 2852, 1753, 1670, 1382, 1255, 1056; $[\alpha]_D^{23}$ +33.8° ($CHCl_3$; *c* 0.07).

3.7. Turraparvin D (5.4 mg), 7

White crystalline, mp 131–133 °C, HRMS (rel. int.) *m/z*: 467.2662 $[M]^+$ ($C_{28}H_{37}NO_5$ req. 467.2672, 1),

449.2566 $[M–H_2O]^+$ (2), 4O7.2460 $[M–CH_3COOH]^+$ (41), 421 (10), 406 (16), 392 (80), 374 (74), 313 (7), 252 (28), 227 (100), 188 (22), 137 (61), 135 (29) and 82 (69); IR: ν_{max}(NaCl) cm^{-1}: 2923, 2856, 1730, 1249, 1137; $[\alpha]_D^{23}$ $+29.8^\circ$ ($CHCl_3$; *c* 0.08).

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