Tirucallane Triterpenoid Saponins from *Munronia delavayi* FRANCH

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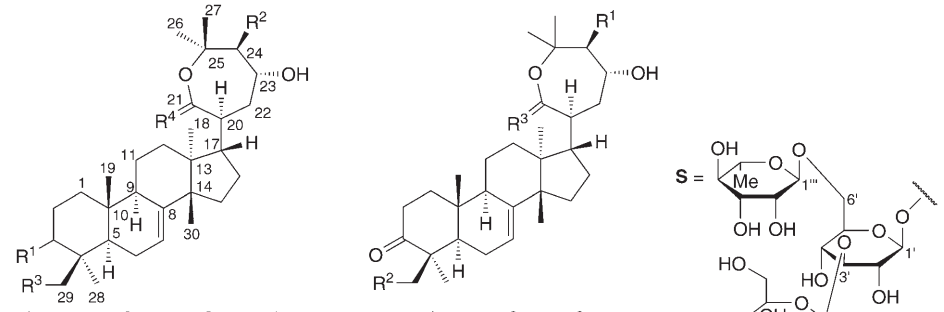
Four new tirucallane triterpenoid saponins, named munronosides I–IV (**2**–**5**), along with three known triterpenoids, sapelin B (**1**), melianodiol, and (3β)-22,23-epoxytirucall-7-ene-3,24,25-triol, were isolated from the EtOH extract of the whole plants of *Munronia delavayi* FRANCH by chromatographic methods. On the basis of spectroscopic evidences, the structures of **2**–**5** were elucidated as (20*S*,23*R*,24*S*)-21,25-epoxy-29-{{*O*-β-D-glucopyranosyl-(1 → 3)-*O*-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-23,24-dihydroxytirucall-7-ene-3,21-dione (**2**), (3β,20*S*,23*R*,24*S*)-21,25-epoxy-29-{{*O*-β-D-glucopyranosyl-(1 → 3)-*O*-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-3,23,24-trihydroxytirucall-7-en-21-one (**3**), (20*S*,23*R*,24*S*)-24-(acetyloxy)-21,25-epoxy-29-{{*O*-β-D-glucopyranosyl-(1 → 3)-*O*-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-23-hydroxytirucall-7-ene-3,21-dione (**4**), and (3β,20*S*,23*R*,24*S*)-24-(acetyloxy)-21,25-epoxy-29-{{*O*-β-D-glucopyranosyl-(1 → 3)-*O*-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-3,23-dihydroxytirucall-7-en-21-one (**5**).

Introduction. – Plants of the family Meliaceae are a promising source of unique natural products for integrated pest management [1]. Plants of the genus *Munronia* are shrubs or half-shrubs which are naturally distributed in Sri Lanka, India, China, Indonesia, and from East Timor to the Philippines [2]. We previously studied *Munronia henryi* HARMS collected from Xishuangbanna, in the south of Yunnan Province where the climate is warm and moist; many novel limonoids have been isolated, and some of them showed significant antifeedant properties [3]. Another species, *Munronia delavayi* FRANCH is narrowly distributed over the rocky area in the northeast of Yunnan Province. The markedly different plant habitats of the two species prompted us to investigate *M. delavayi* to see if the two plants differ in their secondary metabolites. Instead of limonoids as found in *M. henryi*, tirucallane triterpenoids, sapelin B (**1**) [4], melianodiol [5], (3β)-22,23-epoxytirucall-7-ene-3,24,25-triol [6], and four new tirucallane glycosides, munronosides I–IV (**2** – **5**) were isolated from the EtOH extract of *M. delavayi* FRANCH. This paper describes the isolation and structural determination of the new compounds.

Results and Discussion. – Compound **2** was found to possess the molecular formula $C_{48}H_{76}O_{20}$ as evidenced by a quasimolecular-ion peak $[M-H]^-$ at *m*/*z* 971.4836 in the HR-ESI-MS. The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*) and DEPT spectra showed the presence of three sugar units, a rhamnose and two glucose units. The identification of the sugar residues was confirmed by acid hydrolysis of **2** with 10% HCl solution. L-Rhamnose and D-glucose were identified in the hydrolysate by TLC comparison with



1 R^1 = α-OH, R^2 = OH, R^3 = H, R^4 = H,H
3 R^1 = β-OH, R^2 = OH, R^3 = **S**, R^4 = O
5 R^1 = β-OH, R^2 = AcO, R^3 = **S**, R^4 = O

6 R^1 = OH, R^2 = H, R^3 = H,H
2 R^1 = OH, R^2 = **S**, R^3 = O
4 R^1 = AcO, R^2 = **S**, R^3 = O

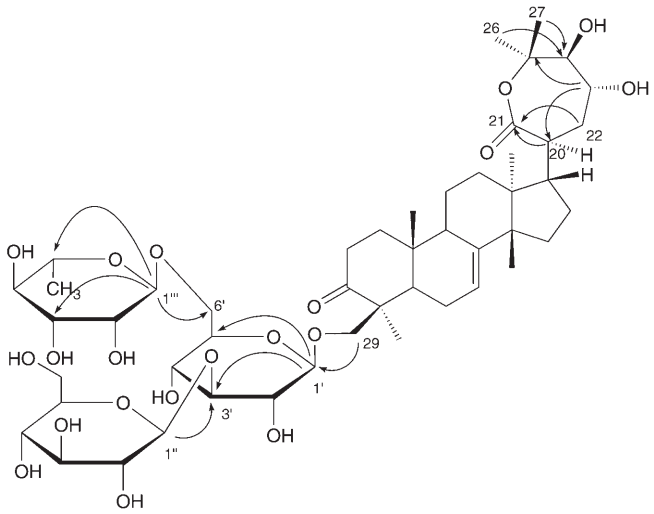


Figure. *Key HMBC Correlations of* **2**

authentic samples and determination of their specific optical rotation [7]. Comparison of the ^{13}C-NMR and DEPT spectra of **2** with those of sapelin B (**1**) and hispidone (**6**) [8] and HMBC (*Fig.*), HSQC, ^{1}H,^{1}H-COSY, and ROESY data allowed to determine the structure of **2** as (20*S*,23*R*,24*S*)-21,25-epoxy-29-{{*O*-β-D-glucopyranosyl-(1 → 3)-*O*-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-23,24-dihydroxytirucall-7-ene-3,21-dione, which was named munronoside I.

The four ^{1}H-NMR signals of **2** at δ(H) 4.82 (*s*, 1 H), 4.65 (*d*, J = 8.0 Hz, 1 H), 4.37 (*d*, J = 7.5 Hz, 1 H), and 1.34 (*d*, J = 6.0 Hz, 3 H), the ^{13}C-NMR signals of three anomeric C-atoms (δ(C) 104.5 (*d*), 102.5 (*d*), and 102.0 (*d*)), of a Me (δ(C) 18.3), two CH_2 (δ(C) 68.0 and 62.3), and 12 CH groups (δ(C) *ca.* 69–82) were consistent with a rhamnose and two glucose units. The *s* at δ(H) 4.82 indicated the α-orientation of the anomeric proton of L-rhamnose. Likewise, the J values of the other two anomeric protons of the sugar moieties revealed the β-configuration of the glucose residues.

Table 1. *^{13}C-NMR Data of Compounds* **2**, **4**, *and* **5** (100 MHz), *and of* **3** (125 MHz)

	2 (CD_3OD)	**3** (CD_3OD)	**4** (C_5D_5N)	**5** (CD_3OD)
C(1)	40.7 (*t*)	38.6 (*t*)	39.5 (*t*)	38.6 (*t*)
C(2)	37.1 (*t*)	29.2 (*t*)	36.7 (*t*)	29.2 (*t*)
C(3)	217.7 (*s*)	81.4 (*d*)	214.9 (*s*)	81.4 (*d*)
C(4)	53.8 (*s*)	42.9 (*s*)	53.2 (*s*)	42.9 (*s*)
C(5)	55.8 (*d*)	53.5 (*d*)	55.0 (*d*)	53.5 (*d*)
C(6)	24.7 (*t*)	24.7 (*t*)	24.2 (*t*)	24.7 (*t*)
C(7)	119.3 (*t*)	119.2 (*d*)	118.7 (*d*)	119.2 (*d*)
C(8)	146.9 (*s*)	146.5 (*s*)	145.9 (*s*)	146.4 (*s*)
C(9)	49.2 (*d*)	50.4 (*d*)	48.2 (*d*)	48.6 (*d*)
C(10)	36.5 (*s*)	35.9 (*s*)	35.6 (*s*)	35.9 (*s*)
C(11)	18.8 (*t*)	18.8 (*t*)	18.8 (*t*)	18.8 (*t*)
C(12)	32.1 (*t*)	32.2 (*t*)	31.5 (*t*)	31.9 (*t*)
C(13)	44.7 (*s*)	44.8 (*s*)	44.1 (*s*)	44.8 (*s*)
C(14)	51.5 (*s*)	51.6 (*s*)	50.8 (*s*)	51.5 (*s*)
C(15)	34.9 (*t*)	34.9 (*t*)	34.3 (*t*)	34.8 (*t*)
C(16)	26.0 (*t*)	25.3 (*t*)	25.5 (*t*)	25.3 (*t*)
C(17)	48.4 (*d*)	48.4 (*d*)	47.7 (*d*)	48.4 (*d*)
C(18)	23.9 (*q*)	23.9 (*q*)	23.5 (*q*)	23.8 (*q*)
C(19)	14.2 (*q*)	14.5 (*q*)	13.8 (*q*)	14.5 (*q*)
C(20)	41.5 (*d*)	41.6 (*d*)	41.1 (*d*)	41.4 (*d*)
C(21)	181.2 (*s*)	181.3 (*s*)	178.4 (*s*)	180.5 (*s*)
C(22)	31.6 (*t*)	31.6 (*t*)	32.1 (*t*)	32.2 (*t*)
C(23)	76.4 (*d*)	76.7 (*d*)	76.6 (*d*)	76.6 (*d*)
C(24)	78.8 (*d*)	79.0 (*d*)	79.5 (*d*)	79.6 (*d*)
C(25)	73.4 (*s*)	73.4 (*s*)	71.3 (*s*)	72.1 (*s*)
C(26)	25.0 (*q*)	25.0 (*q*)	25.9 (*q*)	25.5 (*q*)
C(27)	27.8 (*q*)	27.8 (*q*)	28.4 (*q*)	27.5 (*q*)
C(28)	20.7 (*q*)	23.1 (*q*)	20.8 (*q*)	23.1 (*q*)
C(29)	73.5 (*t*)	71.9 (*t*)	72.8 (*t*)	71.9 (*t*)
C(30)	28.0 (*q*)	27.8 (*q*)	27.6 (*q*)	27.8 (*q*)
AcO			171.0 (*s*), 21.0 (*q*)	172.3 (*s*), 20.9 (*q*)
C(1′)	102.0 (*d*)	101.9 (*d*)	102.6 (*d*)	101.9 (*d*)
C(2′)	77.6 (*d*)	77.8 (*d*)	76.9 (*d*)	77.4 (*d*)
C(3′)	81.4 (*d*)	82.8 (*d*)	82.2 (*d*)	82.8 (*d*)
C(4′)	71.1 (*d*)	71.0 (*d*)	71.3 (*d*)	71.0 (*d*)
C(5′)	78.1 (*d*)	78.2 (*d*)	78.5 (*d*)	78.0 (*d*)
C(6′)	68.0 (*t*)	67.4 (*t*)	68.4 (*t*)	67.4 (*t*)
C(1″)	104.5 (*d*)	105.3 (*d*)	105.7 (*d*)	105.3 (*d*)
C(2″)	78.4 (*d*)	78.5 (*d*)	78.7 (*d*)	78.2 (*d*)
C(3″)	75.9 (*d*)	75.7 (*d*)	76.6 (*d*)	75.6 (*d*)
C(4″)	77.9 (*d*)	78.0 (*d*)	78.3 (*d*)	77.8 (*d*)
C(5″)	72.2 (*d*)	72.3 (*d*)	72.8 (*d*)	72.4 (*d*)
C(6″)	62.3 (*t*)	61.9 (*t*)	62.6 (*t*)	61.9 (*t*)
C(1‴)	102.5 (*d*)	102.0 (*d*)	102.7 (*d*)	102.0 (*d*)
C(2‴)	73.8 (*d*)	73.9 (*d*)	74.0 (*d*)	73.9 (*d*)
C(3‴)	72.0 (*d*)	72.1 (*d*)	72.4 (*d*)	72.3 (*d*)
C(4‴)	70.9 (*d*)	70.3 (*d*)	71.3 (*d*)	70.3 (*d*)
C(5‴)	69.7 (*d*)	69.7 (*d*)	69.9 (*d*)	69.7 (*d*)
C(6‴)	18.3 (*q*)	18.2 (*q*)	18.8 (*q*)	18.2 (*q*)

Table 2. *^{1}H-NMR Data* (500 MHz) *of Compounds* **2**–**5**. δ in ppm, J in Hz.

	2 (CD_3OD)	**3** (CD_3OD)	**4** (C_5D_5N)	**5** (CD_3OD)
CH_2(1)	1.50–1.53 (*m*), 2.14–2.18 (*m*)	1.25–1.30 (*m*), 1.71–1.75 (*m*)	1.25–1.29 (*m*), 1.81–1.85 (*m*)	1.20–1.24 (*m*), 1.73–1.77 (*m*)
CH_2(2)	2.29–2.31 (*m*), 2.99–3.02 (*m*)	1.72–1.77 (*m*)	1.96–2.00 (*m*), 3.22–3.26 (*m*)	1.75–1.79 (*m*)
H–C(3)	–	3.23 (*dd*, J = 8.0, 4.5)	–	3.23 (*dd*, J = 8.0, 4.0)
H–C(5)	1.76–1.80 (*m*)	1.45 (*dd*, J = 2.5, 7.0)	1.76–1.80 (*m*)	1.47–1.52 (*m*)
CH_2(6)	1.60–1.64 (*m*), 1.81–1.84 (*m*)	1.54–1.57 (*m*), 1.77–1.80 (*m*)	1.44–1.50 (*m*), 1.76–1.81 (*m*)	1.45–1.51 (*m*), 1.77–1.82 (*m*)
H–C(7)	5.38 (br. *s*)	5.27 (br. *s*)	5.22 (br. *s*)	5.28 (br. *s*)
H–C(9)	2.42–2.46 (*m*)	2.25–2.29 (*m*)	2.26–2.30 (*m*)	2.27–2.32 (*m*)
CH_2(11)	1.70–1.73 (*m*), 1.78–1.81 (*m*)	1.60–1.55 (*m*)	1.44–1.49 (*m*)	1.65–1.58 (*m*)
CH_2(12)	1.78–1.82 (*m*)	1.74–1.82 (*m*)	1.80–1.84 (*m*)	1.73–1.79 (*m*)
CH_2(15)	1.63–1.66 (*m*)	1.53–1.58 (*m*)	1.45–1.56 (*m*)	1.55–1.61 (*m*)
CH_2(16)	2.14–2.18 (*m*), 2.28–2.31 (*m*)	1.90–1.95 (*m*), 2.23–2.29 (*m*)	2.12–2.16 (*m*), 2.22–2.28 (*m*)	1.95–2.01 (*m*), 2.22–2.27 (*m*)
H–C(17)	2.40–2.43 (*m*)	2.30–2.35 (*m*)	1.91–1.95 (*m*)	2.29–2.33 (*m*)
Me(18)	0.92 (*s*)	0.86 (*s*)	0.87 (*s*)	0.84 (*s*)
Me(19)	1.19 (*s*)	0.76 (*s*)	1.02 (*s*)	0.77 (*s*)
H–C(20)	2.84–2.88 (*m*)	2.79–2.82 (*m*)	2.80–2.85 (*m*)	2.79–2.82 (*m*)
CH_2(22)	2.33–2.35 (*m*), 2.26–2.30 (*m*)	2.18–2.22 (*m*), 2.26–2.30 (*m*)	2.22–2.26 (*m*), 2.49–2.54 (*m*)	1.83–1.89 (*m*), 2.38–2.43 (*m*)
H–C(23)	3.43–3.47 (*m*)	3.40–3.45 (*m*)	5.09–5.14 (*m*)	3.38–3.42 (*m*)
H–C(24)	3.37 (br. *s*)	3.27 (br. *s*)	5.40 (*d*, J = 5.0)	4.80 (*d*, J = 5.0)
Me(26)	1.29 (*s*)	1.23 (*s*)	1.56 (*s*)	1.27 (*s*)
Me(27)	1.34 (*s*)	1.34 (*s*)	1.51 (*s*)	1.22 (*s*)
Me(28)	1.21 (*s*)	1.21 (*s*)	1.39 (*s*)	1.22 (*s*)
CH_2(29)	3.80 (*d*, J = 10.0), 4.27 (*d*, J = 10.0)	3.98 (*d*, J = 10.0), 4.03 (*d*, J = 10.0)	4.42 (*d*, J = 10.0), 4.45 (*d*, J = 10.0)	3.99 (*d*, J = 10.0), 4.02 (*d*, J = 10.0)
Me(30)	1.14 (*s*)	1.04 (*s*)	0.96 (*s*)	1.04 (*s*)
AcO	–	–	2.12 (*s*)	2.12 (*s*)
H–C(1′)	4.37 (*d*, J = 7.5)	4.38 (*d*, J = 8.0)	4.79 (*d*, J = 8.0)	4.39 (*d*, J = 7.5)
H–C(2′)	3.42–3.45 (*m*)	3.38–3.42 (*m*)	3.93–3.95 (*m*)	3.73–3.77 (*m*)
H–C(3′)	3.23–3.27 (*m*)	3.39–3.43 (*m*)	4.12–4.16 (*m*)	3.35–3.79 (*m*)
H–C(4′)	3.37–3.41 (*m*)	3.39–3.42 (*m*)	3.89–3.92 (*m*)	3.38–3.42 (*m*)
H–C(5′)	3.62–3.66 (*m*)	3.59 (*t*, J = 7.5)	4.23–4.26 (*m*)	3.19–3.24 (*m*)
CH_2(6′)	4.01–4.05 (*m*), 3.68–3.72 (*m*)	3.94–4.00 (*m*), 3.68–3.73 (*m*)	4.12–4.16 (*m*), 4.55–4.59 (*m*)	3.93–3.98 (*m*), 3.70–3.75 (*m*)
H–C(1″)	4.65 (*d*, J = 8.0)	4.62 (*d*, J = 7.5)	5.35 (*d*, J = 7.5)	4.62 (*d*, J = 8.0)
H–C(2″)	3.68–3.72 (*m*)	3.68–3.72 (*m*)	3.91–3.95 (*m*)	3.58–3.62 (*m*)
H–C(3″)	3.35–3.38 (*m*)	3.22–3.27 (*m*)	4.10–4.15 (*m*)	3.20–3.23 (*m*)
H–C(4″)	3.30–3.34 (*m*)	3.20–3.26 (*m*)	4.23–4.27 (*m*)	3.35–3.40 (*m*)
H–C(5″)	3.74–3.78 (*m*)	3.66–3.70 (*m*)	4.22–4.26 (*m*)	3.68–3.73 (*m*)
CH_2(6″)	3.91–3.95 (*m*), 3.81–3.85 (*m*)	3.78–3.82 (*m*), 3.70–3.75 (*m*)	4.55–4.59 (*m*), 4.43–4.48 (*m*)	3.78–3.83 (*m*), 3.71–3.75 (*m*)
H–C(1‴)	4.82 (*s*)	4.75 (*s*)	5.45 (*s*)	4.76 (*s*)
H–C(2‴)	3.41–3.45 (*m*)	3.40–3.43 (*m*)	4.23–4.27 (*m*)	3.35–3.39 (*m*)
H–C(3‴)	3.73–3.77 (*m*)	3.81–3.85 (*m*)	4.51–4.56 (*m*)	3.80–3.85 (*m*)
H–C(4‴)	3.41–3.45 (*m*)	3.41–3.45 (*m*)	4.25–4.29 (*m*)	3.38–3.42 (*m*)
H–C(5‴)	3.73–3.77 (*m*)	3.68–3.72 (*m*)	4.33–4.38 (*m*)	3.68–3.73 (*m*)
Me(6‴)	1.34 (*d*, J = 6.0)	1.28 (*d*, J = 6.0)	1.62 (*d*, J = 6.0)	1.29 (*d*, J = 6.0)

Besides of three sugar units, the ^{13}C-NMR and DEPT spectra of **2** also showed 30 C-atoms, six Me, nine CH_2, and seven CH groups, and eight quaternary C-atoms. These data were similar to those of hispidone (**6**), except for an additional C=O at δ(C) 181.2 (*s*) and the loss of a Me group in **2**. This C=O group was located at C(21) by correlations between its δ(C) 181.2 (*s*) and δ(H) 2.26–2.35 (2*m*, CH_2(22)) and 2.84–2.88 (*m*, H–C(20)) in the HMBC spectrum (*Fig.*). Signals at δ(H) 3.80 and 4.27 (each *d*, J = 10.0 Hz, each 1 H) corresponding to δ(C) 73.5 (*t*) in its HSQC plot showed cross-peaks with δ(C) 217.7 (*s*, C(3)), 102.0 (*d*, C(1′)), 55.8 (*d*, C(5)), and 20.7 (*q*, C(28)), which suggested that O-substitution took place at C(29) (δ(C) 73.5 (*t*)). A ROESY correlation δ(H) 1.76–1.80 (*m*, H–C(5))/δ(H) 1.21 (*s*, Me(28)) confirmed the CH_2(29)–O group. On the basis of the NOE correlations δ(H) 3.43–3.47 (*m*, H–C(23))/δ(H) 1.34 (*s*, Me(27)) and δ(H) 3.37 (br.*s*, H–C(24))/δ(H) 1.29 (*s*, Me(26)), the configuration of OH–C(23) and OH–C(24) were determined to be *trans*. The glycosylation position was unambiguously determined to be at C(29) from the HMBC cross-peak δ(H) 4.37 (*d*, J = 7.5 Hz, H–C(1′))/δ(C) 73.5 (C(29)). HMBC Cross-peaks δ(H) 4.37 (H–C(1′))/δ(C) 81.4 (*d*) and 78.1 (*d*) showed the two latter signals arising from C(3′) and C(5′), respectively. ^{1}H,^{1}H-COSY Cross-peaks δ(H) 3.62–3.66 (*m*, H–C(5′))/δ(H) 4.01–4.05 and 3.68–3.72 (2 *m*, CH_2(6′)), and the HSQC data enabled to assign δ(C) 68.0 (*t*) to C(6′). On the basis of the correlations δ(H) 4.65 (*d*, J = 8.0 Hz, H–C(1″)), δ(C) 81.4 (*d*, C(3′)) and δ(H) 4.82 (*s*, H–C(1‴)), δ(C) 68.0 (*t*, C(6′)), the presence of a glucopyranosyl-(1 → 3)-[rhamnopyranosyl-(1 → 6)]-glucopyranosyl moiety was deduced.

Compound **3** has the molecular formula $C_{48}H_{78}O_{20}$ as deduced from the quasimolecular-ion peak $[M-H]^-$ at m/z 973.5021 in the HR-ESI-MS. The structure of **3** was deduced to be (3*β*,20*S*,23*R*,24*S*)-21,25-epoxy-29-{{*O*-*β*-D-glucopyranosyl-(1 → 3)-*O*-[*α*-L-rhamnopyranosyl-(1 → 6)]-*β*-D-glucopyranosyl}oxy}-3,23,24-trihydroxytirucall-7-en-21-one, by comparison with the data of **2**, and named munronoside II.

The ^{13}C-NMR (*Table 1*) and DEPT spectra of **3** displayed similarities to those of **2**, except for the absence of the signal at δ(C) 217.7 (*s*, C(3)) in **3** which was replaced by δ(C) 81.4 (*d*, C(3)), indicating an OH substitution at C(3). This assumption was supported by the HMBC cross-peaks δ(H) 3.23 (*dd*, J = 8.0, 4.5 Hz, H–C(3))/δ(C) 23.1 (*q*, C(28)), 42.9 (*s*, C(4)), and 53.5 (*d*, C(5)). The large coupling constant of H–C(3) (*Table 2*) indicated the *β*-orientation of the OH group [9].

Compound **4** possesses the molecular formula $C_{50}H_{78}O_{20}$ as shown by the quasimolecular-ion peak $[M-H]^-$ at m/z 1013.4946 in the HR-ESI-MS. The structure of **4** was deduced to be (20*S*,23*R*,24*S*)-24-(acetyloxy)-21,25-epoxy-29-{{*O*-*β*-D-glucopyranosyl-(1 → 3)-*O*-[*α*-L-rhamnopyranosyl-(1 → 6)]-*β*-D-glucopyranosyl}oxy}-23-hydroxytirucall-7-ene-3,21-dione and named munronoside III.

The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*) and DEPT spectra of **4** displayed similarities to those of **2**, except for additional signals of an AcO group (δ(C) 171.0 (*s*) and 21.0 (*q*)). Location of the AcO group could be assigned to C(24) by the HMBC cross-peak δ(C) 171.0 (*s*)/δ(H) 5.40 (*d*, J = 5.0 Hz, H–C(24)).

Compound **5** was found to possess the molecular formula $C_{50}H_{80}O_{21}$ as evidenced by a quasimolecular ion peak $[M-H]^-$ at m/z 1015.5097 in the HR-ESI-MS. The structure of **5** was deduced to be (3*β*,20*S*,23*R*,24*S*)-24-(acetyloxy)-21,25-epoxy-29-{{*O*-*β*-D-glucopyranosyl-(1 → 3)-*O*-[*α*-L-rhamnopyranosyl-(1 → 6)]-*β*-D-glucopyranosyl}oxy}-3,23-dihydroxytirucall-7-en-21-one and named munronoside IV.

The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*) and DEPT spectra of **5** showed similarities to those of **3**, except for an additional AcO group (δ(C) 172.3 (*s*) and 20.9 (*q*)). The AcO group was located at C(24), as in **4** as established by from the HMBC cross-peak δ(C) 172.3 (*s*)/δ(H) 4.80 (*d*, J = 5.0 Hz, H–C(24).

Compounds **2**–**5** all possess a new aglycone differing from previously reported compounds, in particular in the presence of an oxo substituent at C(21). The configuration of OH–C(3) in **3** and **5** is β instead of α, and an AcO group replaces the OH group at C(24) in the case of **4** and **5**.

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Experimental Part

General. Column chromatography (CC): Silica gel (200–300 mesh; *Qindao Marine Chemical Factory*, Qindao, China). TLC: Silica gel GF_{254} (*Qindao Marine Chemical Factory*); detection by spraying with 5% H_2SO_4 soln. and heating of the plate. Optical rotations: *Horiba SEAP-300* spectropolarimeter IR Spetra: $\tilde{\nu}$ in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AM-400* and *DRX-500* NMR spectrometer; $SiMe_4$ as internal standard, δ in ppm, J in Hz. MS: *VG Autospec-3000* and *Finnigan MAT-90* spectrometers for FAB, and *API Qstar-Pulsar-1* spectrometer for HR-ESI; in m/z (rel.%).

Plant Material. The whole plant of *M. delavayi* FRANCH was collected in QianJia County, Yunnan Province, People's Republic of China, in May 2004, and identified by Mr. *Li-Shan Xie*, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No.0848852) was deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried whole plant (11.5 kg) was crushed and extracted with 90% aq. EtOH (4 × 40 l) at r.t. (4 × 48 h). After evaporation of the EtOH, the viscous residue was partitioned with AcOEt (4 × 15 l) to afford an AcOEt and an H_2O extract. The AcOEt extract (210 g) was subjected to CC (silica gel (2.0 kg), $CHCl_3/Me_2CO$ 1:0 → 1:1): *Fractions I-VIII*. *Fr. VI* (21.0 g) was subjected to CC (silica gel (600 g), petroleum ether/Me_2CO 3:1): **1** (21 mg) and melianodiol (28 mg). *Fr. VII* (15.5 g) was subjected to CC (silica gel, $CHCl_3/Me_2CO$ 8:2): (3β)-22,23-Epoxytirucall-7-ene-3,24,25-triol (25 mg). The H_2O extract (see above) was partitioned with butan-1-ol. After evaporation of the butan-1-ol, the residue (280 g) was subjected to CC (silica gel (3.0 kg), $CHCl_3$/MeOH 9:1 → 2:1): *Fr. IX–XIII*. *Fr. XI* (14 g) was subjected to CC (*RP-18* (300 g), MeOH/H_2O 4:6 → 6:4): **2** (75 mg), **3** (56 mg), **4** (32 mg), and **5** (65 mg).

*(20*S*,23*R*,24*S*)-21,25-Epoxy-29-{{*O*-β-D-glucopyranosyl-(1 → 3)-O-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-23,24-dihydroxytirucall-7-ene-3,21-dione (=(4β,13α,14β,17α,20*S*,23*R*,24*S*)-29-{{O-6-Deoxy-α-L-mannopyranosyl-(1 → 6)-O-[β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranosyl}oxy}-21,25-epoxy-23,24-dihydroxylanost-7-ene-3,21-dione*; **2**): White powder. $[\alpha]_D^{22} = -68.7$ ($c = 0.12$, MeOH). IR (KBr): 3424, 2935, 1762, 1703, 1637. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (glycerol; neg.): 971 (100, $[M-H]^-$). HR-ESI-MS: 971.4836 ($C_{48}H_{75}O_{20}^-$; calc. 971.4851).

*(3β,20*S*,23*R*,24*S*)-21,25-Epoxy-29-{{O-β-D-glucopyranosyl-(1 → 3)-O-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-3,23,24-trihydroxytirucall-7-en-21-one (=(3β,4β,13α,14β,17α,20*S*,23*R*,24*S*)-29-{{O-6-Deoxy-α-L-mannopyranosyl-(1 → 6)-O-[β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranosyl}oxy}-21,25-epoxy-3,23,24-trihydroxylanost-7-en-21-one*; **3**): White powder. $[\alpha]_D^{22} = -57.6$ ($c = 0.17$, MeOH). IR (KBr): 3423, 2932, 1760, 1740. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (glycerol; neg.): 973 (100, $[M-H]^-$). HR-ESI-MS: 973.5021 ($C_{48}H_{77}O_{20}^+$, calc. 973.5008).

*(20*S*,23*R*,24*S*)-24-(Acetyloxy)-21,25-epoxy-29-{{O-β-D-glucopyranosyl-(1 → 3)-O-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl}oxy}-23-hydroxytirucall-7-ene-3,21-dione (=(3β,4β,13α,14β,17α,20*S*,23*R*,24*S*)-24-(Acetyloxy)-29-{{O-β-deoxy-α-L-mannopyranosyl-(1 → 6)-O-[β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranosyl}oxy}-21,25-epoxy-23-hydroxylanost-7-ene-3,21-dione*; **4**): White powder. $[\alpha]_D^{22} = -58.9$ ($c = 0.15$, MeOH). IR (KBr): 3430, 2936, 1748, 1706. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (glycerol; neg.): 1013 (100, $[M-H]^-$). HR-ESI-MS: 1013.4946 ($C_{50}H_{77}O_{21}^-$, calc. 1013.4957).

(3β,20S,23R,24S)-24-(Acetyloxy)-21,25-epoxy-29-{[O-β-D-glucopyranosyl-(1 → 3)-O-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranosyl]oxy}-3,23-dihydroxytirucall-7-en-21-one (=(3β,4β,13α,14β,17α,20S,23R,24S)-24-(Acetyloxy)-29-{[O-6-deoxy-α-L-mannopyranosyl-(1 → 6)-O-[β-D-glucopyranosyl-(1 → 3)]-β-D-glucopyranosyl]oxy}-21,25-epoxy-3,23-dihydroxylanost-7-en-21-one; **5**): White powder. $[\alpha]_D^{22} = -37.8$ ($c = 0.15$, MeOH). IR (KBr): 3424, 2933, 1749, 1638. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (glycerol): 1015 (100, $[M-H]^-$). HR-ESI-MS: 1015.5097 ($C_{50}H_{79}O_{21}^-$; calc. 1015.5113).

Acid Hydrolysis of **2**–**5**. Compounds **2**–**5** (15 mg each) were refluxed with 10% HCl/MeOH (20 ml) at 80° for 6 h. After cooling, the mixture was concentrated and the residue partitioned with AcOEt/H_2O. The sugars in this mixture were identified as glucose and rhamnose by TLC comparison (MeCOEt/^{i}PrOH/Me_2CO/H_2O 20:10:7:6). Separation of the residue of the H_2O layer was performed by prep. TLC (4× elution with $CHCl_3$/MeOH/H_2O 70:30:1): D-glucose (R_f 0.50) and L-rhamnose (R_f 0.67), with positive values of the specific rotation ($[\alpha]_D = 19.2$, 21.5, 24.6, and 24.0, and $[\alpha]_D = 26.5$, 25.0, 21.5, and 21.6, resp.) The residue of the AcOEt layer was analyzed by HP-TLC (silica gel GF_{254} plate, $CHCl_3$/Me_2CO 3:1 and petroleum ether/$CHCl_3$ 3:1): Several decomposition products.

REFERENCES

[1] H. Greger, T. Pacher, B. Brem, M. Bacher, O. Hofer, *Phytochemistry* **2001**, *57*, 57.
[2] Yunnan Institute of Botany, 'Flora of Yunnanica, Tomus 1', Science Press, Beijing, 1977, p. 214.
[3] S. H. Qi, D. G. Wu, L. Chen, Y. B. Ma, X. D. Luo, *J. Asian Nat. Prod. Res.* **2003**, *5*, 215; S. H. Qi, D. G. Wu, L. Chen, Y. B. Ma, X. D. Luo, *Tetrahedron* **2003**, *59*, 4193; S. H. Qi, D. G. Wu, L. Chen, Y. B. Ma, X. D. Luo, *J. Agric. Food Chem.* **2003**, *51*, 6949.
[4] W. R. Chan, D. R. Taylor, T. H. Yee, *J. Chem. Soc., C* **1970**, 311.
[5] D. A. G. Cortez, P. C. Vieira, J. B. Fernandes, G. F. G. F. da Silva, A. G. Ferreira, *Phytochemistry* **1992**, *31*, 625.
[6] X. D. Luo, S. H. Wu, Y. B. Ma, D. G. Wu, *Phytochemistry* **2000**, *54*, 801.
[7] J. Eskander, C. Lavaud, S. M. Abdel-khalik, H. S. M. Soliman, I. I. Mahmoud, C. Long, *J. Nat. Prod.* **2005**, *68*, 832.
[8] H. Itokawa, E. Kishi, H. Morita, K. Takeya, *Chem. Pharm. Bull.* **1992**, *40*, 1053.
[9] X. H. Cai, X. D. Luo, J. Zhou, X. J. Hao, *Org. Lett.* **2005**, *7*, 2877.

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