

## Insect Antifeedants from *Munronia henryi*: Structure of Munroniamide

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A novel A,B-seco-tetranortriterpenoid lactam, named munroniamide (**1**), along with three known ceramides (**2–4**), was isolated from the methanolic extract of the whole bodies of *Munronia henryi*. The structure of **1** was established using spectroscopic methods. Compound **2** exhibited significant antifeeding activity, and **1** exhibited moderate activity, whereas **3** and **4** showed negative activity against *Pieris brassicae* L.

**KEYWORDS:** *Munronia henryi*; tetranortriterpenoid lactam; ceramides; antifeedants; *Pieris brassicae*

### INTRODUCTION

Recently, tetranortriterpenoids (limonoids) have attracted much attention because of the marked insect antifeeding and growth-regulating activity of azadirachtin. Tetranortriterpenoids are diverse and abundant in members of the family Meliaceae. Many papers about tetranortriterpenoids isolated from the family Meliaceae have discussed their roles in antifeeding (1–3), cytotoxicity (4–6), ichthyotoxicity (7), insect growth inhibition (8), inhibition of cell adhesion (9, 10), and larval growth (11). The genus *Munronia* Wight (Meliaceae), comprising 13–15 species, is naturally distributed in China, Sri Lanka, India, Indonesia, and The Philippines. No chemical constituents have been published for this genus to the present. Three species of this genus have been found in Yunnan province. *M. henryi* Harms is a low, small semibush, which has been used for the treatment of many diseases such as tuberculosis, colds, indigestion, and sore throat in Chinese traditional medicine (12). Moreover, *M. henryi* is also used as a pest control agent in rural areas of Yunnan province.

As part of a program seeking novel antifeeding tetranortriterpenoids from Meliaceae plants (13–18), we undertook an investigation of *M. henryi*. A novel tetranortriterpenoid lactam, munroniamide (**1**), together with three known ceramides, 1-*O*- $\beta$ -D-glucopyranosyl-(2*S*,3*S*,4*R*,8*Z*)-2-*N*-(2'-hydroxytetracosanoyl)-heptadecaspingia-8-ene (**2**) (19), (2*S*,3*S*,4*R*,8*E*)-2-*N*-(2'-hydroxytetracosanoyl)heptadecaspingia-8-ene (**3**) (20), and (2*S*,3*R*,4*E*)-2-*N*-(2'-hydroxytetracosanoyl)heptadecaspingia-4-ene (**4**) (21),

was isolated from whole-plant material of *M. henryi*. The structure of **1** was elucidated on the basis of extensive 1D and 2D NMR experiments. Compounds **1–4** were subjected to an antifeedant assay of *Pieris brassicae* L.

### MATERIALS AND METHODS

**General Experimental Procedures.** All of the melting points were obtained on an XRC-1 micromelting apparatus and are uncorrected. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH solution. IR (KBr) spectra were obtained on a Bio-Rad FTS-135 infrared spectrophotometer. <sup>1</sup>H, <sup>13</sup>C, and 2D NMR spectra were recorded on a Bruker AM-400 and a DRX-500 MHz NMR spectrometer with TMS as internal standard. MS spectral data were obtained on a VG Autospec-3000 spectrometer, 70 eV for EI. Silica gel (200–300 mesh) for column chromatography and GF<sub>254</sub> for TLC were obtained from the Qindao Marine Chemical Factory, Qindao, People's Republic of China.

**Extraction and Isolation.** *M. henryi* plants were collected from Xishuangbanna, Yunnan, People's Republic of China, in December 2001, and identified by Prof. J. Y. Cui, Xishuangbanna Botany Garden, Academia Sinica. A voucher specimen (no. 3386) was deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, Kunming, People's Republic of China. Air-dried and powdered plant materials (4.5 kg) of *M. henryi* were extracted with MeOH three times at room temperature, and the solvent was evaporated in vacuo. The residue was partitioned in H<sub>2</sub>O and extracted with EtOAc three times. The EtOAc extracts were concentrated in vacuo to afford 135 g of residue, which was subjected to column chromatography (CC) on a silica gel, using CHCl<sub>3</sub>/Me<sub>2</sub>CO (from CHCl<sub>3</sub> to CHCl<sub>3</sub>/Me<sub>2</sub>CO 1:1) as eluent. By combining the fractions with TLC (GF<sub>254</sub>) monitoring, 11 fractions were obtained. Then, fraction 5 (15 g) was subjected to column chromatography (CC) on silica gel, eluted with CHCl<sub>3</sub>/Me<sub>2</sub>CO (from 7:3 to 2:1), respectively, to give four subfractions (A–D). Fraction A (5.0 g) was subjected to CC on silica

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Table 1. 1D and 2D NMR Spectral Data of Compound 1<sup>a</sup>

no.	<sup>13</sup> C NMR	<sup>1</sup> H (HMQC)	HMBC	<sup>1</sup> H- <sup>1</sup> H COSY	NOESY
1	148.8 d	6.56 (1H, d, 11.7)	H-2, 9, 19	H-2	
2	125.9 d	6.54 (1H, d, 11.7)	H-1	H-1	
3	168.6 s		H-1, 2, 11		
4	87.2 s		H-5, 28, 29		
5	55.0 d	3.36 (1H, dd, 8.8, 4.5)	H-6, 9, 19, 28, 29	H-6αβ	H-28
6	33.8 t	2.84 (1H, dd, 17.8, 4.5), 3.24 (1H, dd, 17.8, 8.8) 3.24 (1H, dd, 17.8, 8.8, H-6α)	H-5	H-5	
7	175.1 s		H-5, 6, 29		
8	136.9 s		H-9, 30		
9	57.3 d	3.78 (1H, d, 8.1)	H-19, 30	H-11	H-11
10	42.7 s		H-5, 6, 9, 11, 19		
11	80.7 d	4.93 (1H, dd, 10.8, 8.1)	H-9, 12	H-9, 12	H-9, 18
12	75.8 d	6.47 (1H, d, 10.8)	H-9, 11, 18	H-11	H-17, 19
13	45.8 s		H-12, 16, 18		
14	71.5 s		H-9, 18, 30		
15	59.8 d	3.84 (1H, s)	H-16		H-18
16	32.0 t	2.07 (1H, dd, 14.0, 7.3), 2.19 (1H, dd, 14.0, 11.1)	H-15, 17	H-17	
17	39.9 d	3.14 (1H, dd, 10.6, 7.3)	H-15, 18	H-16αβ	H-12
18	13.7 q	0.94 (3H, s)	H-12, 17		H-11, 15
19	22.3 q	1.19 (3H, s)	H-1, 5, 9		H-12, 29
20	137.5 s		H-16, 17, 22, 23		
21	170.9 s		H-17, 22, 23		
22	139.5 d	6.74 (1H, s)	H-17, 23		
23	50.9 t	3.86, 3.78 (each 1H, s)	H-22		
28	30.9 q	1.36 (3H, s)	H-29		H-5
29	26.7 q	1.40 (3H, s)	H-28		H-19
30	120.5	5.28, 5.20 (each 1H, s)	H-9		
CH <sub>3</sub> CO	170.6 s		H-12, CH <sub>3</sub> CO CH <sub>3</sub> COO		
1'	21.2 q	1.96 (3H, s)			
2'	175.3 s		H-23, 2'		
3'	24.6 t	2.48, 2.02 (each 1H, m)	H-3', NH	H-3'	
NH	42.0 t	3.57 (2H, m)	H-2', NH	H-2'	
NH <sub>2</sub>		2.47 (1H, m) 2.00 (2H, m)		NH <sub>2</sub> NH	

<sup>a</sup> Chemical shift values  $\delta$  are in ppm, and coupling constant values  $J$  are in Hz; 400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR, and 500 MHz for 2D NMR in pyridine-*d*<sub>5</sub> with TMS as internal standard.

gel, eluted with CHCl<sub>3</sub>/Me<sub>2</sub>CO (7:3), to give **4** (14 mg). Fraction C (2.2 g) was chromatographed over Sephadex LH-20 eluting with MeOH to afford **3** (26 mg). Fraction 8 was repeatedly subjected to CC on silica gel, eluted with CHCl<sub>3</sub>/MeOH (12:1), to give **1** (36 mg). Fraction 9 was repeatedly subjected to CC on silica gel, eluted with CHCl<sub>3</sub>/MeOH (9:1), to give **2** (21 mg).

**Munroniamide 1**: white powder; mp 338–339 °C; [ $\alpha$ ]<sub>D</sub><sup>27.1</sup> -3.75 (*c* 0.27, pyridine); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 209 (4.39) nm; IR (KBr)  $\nu_{\max}$  3443, 2981, 2943, 1731, 1681, 1642, 1466, 1388, 1370, 1271, 1237, 1174, 1060, 1035, 961 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR spectral data, see **Table 1**; EIMS,  $m/z$  597 [M]<sup>+</sup> (2), 552 (0.6), 537 (2), 511 (2), 497 (2.5), 478 (3), 425 (1.5), 392 (2.5), 364 (3), 344 (10), 298 (11), 285 (7), 256 (6), 239 (10), 223 (20), 207 (17), 195 (27), 178 (25), 165 (24), 149 (26), 122 (31), 108 (35), 97 (70), 81 (57), 69 (100); HREIMS,  $m/z$  597.2670 [M]<sup>+</sup> (calcd for C<sub>31</sub>H<sub>39</sub>N<sub>3</sub>O<sub>9</sub> 597.2686, error = 1.6 ppm).

**Bioassay**. The test compounds were dissolved in acetone (including ~1% of DMSO for improvement of solubility) at concentrations of 1000 ppm, respectively. Leaf disks of *Brassica oleracea* L. (1.5 cm diameter) were dipped in the test solutions, and the control disks were in acetone (including 1% of DMSO) for 1 s. All of the leaf disks were dried before being presented to the insect. The test insects were third-instar larvae of *P. brassicae* L., which had been deprived of food for 6 h prior to being individually placed in a Petri dish. Five Petri dishes, each containing two larvae and three leaf disks, were used for each sample. After 48 h, the areas eaten were measured by an LI-3000 area-measurement apparatus. The antifeedant rate was calculated from [(*C* - *T*)/*C*] × 100%, where *C* and *T* are control disk areas eaten and treated disk areas eaten, respectively. After 6 days, the mortality of the test insects was calculated.

## RESULTS AND DISCUSSION

Compound **1** exhibited a molecular ion peak at  $m/z$  597 in its EIMS, which suggested an odd-number nitrogen atom in **1**.

It possessed a molecular formula of C<sub>31</sub>H<sub>39</sub>N<sub>3</sub>O<sub>9</sub> as determined by HREIMS, which was supported by the <sup>13</sup>C and DEPT NMR spectra. Its UV spectrum exhibited maximum absorption at 209 nm ( $\alpha,\beta$ -unsaturated lactone). The IR spectrum of **1** showed absorption bands for -NH (3443 cm<sup>-1</sup>), a carbonyl group (1731 cm<sup>-1</sup>), an amide group (1681 cm<sup>-1</sup>), and double bonds (1642 cm<sup>-1</sup>). The <sup>13</sup>C NMR and DEPT spectra displayed signals for 31 carbons, namely, 26 skeleton carbons [including 4 tertiary methyl groups, 3 methylenes, 6 methines (2 of which were oxymethines), 4 quaternary carbons, 3 double bonds, and 3 carbonyl groups], an acetyl [ $\delta_C$  170.6 (s), 21.2 (q)], and an acyl radical moiety [ $\delta_C$  175.0 (s), 42.0 (t), 24.6 (t)]. The <sup>1</sup>H NMR spectrum showed five methyl singlets at  $\delta_H$  0.93, 1.19, 1.36, 1.40 (tertiary C-methyl groups), and 1.96 (acetate methyl) and bisubstituting olefinic signals at  $\delta_H$  5.28 and 5.20 (each 1H, s). All of these data suggested that **1** had a tetranortriterpenoid skeleton with a double bond between C-8 and C-30 (17, 22–24).

The <sup>13</sup>C and <sup>1</sup>H NMR spectra showed an oxirane [ $\delta_C$  71.5 (s), 59.8 (d),  $\delta_H$  3.84 (1H, s)], which was assigned to be 14,15-epoxy as for other analogous tetranortriterpenoids (**4**, **14**, **24**). This was further supported by the HMBC spectrum (**Table 1**). A NOE interaction between  $\delta_H$  3.84 (1H, s, H-15) and  $\delta_H$  0.94 (3H, s, H-18) in the NOESY spectrum indicated 14 $\beta$ ,15 $\beta$ -substituents. The olefinic carbons  $\delta_C$  120.5 (t) and 136.9 (s) and corresponding to protons  $\delta_H$  5.28 and 5.20 (each 1H, s) suggested an olefinic linkage between C-8 and C-30. This was confirmed by the HMBC spectrum, which showed correlations of  $\delta_H$  5.28 and 5.20 (each 1H, s, H-30) with  $\delta_C$  57.3 (d, C-9) and 71.5 (s, C-14). An acetoxy was placed at C-12 by the

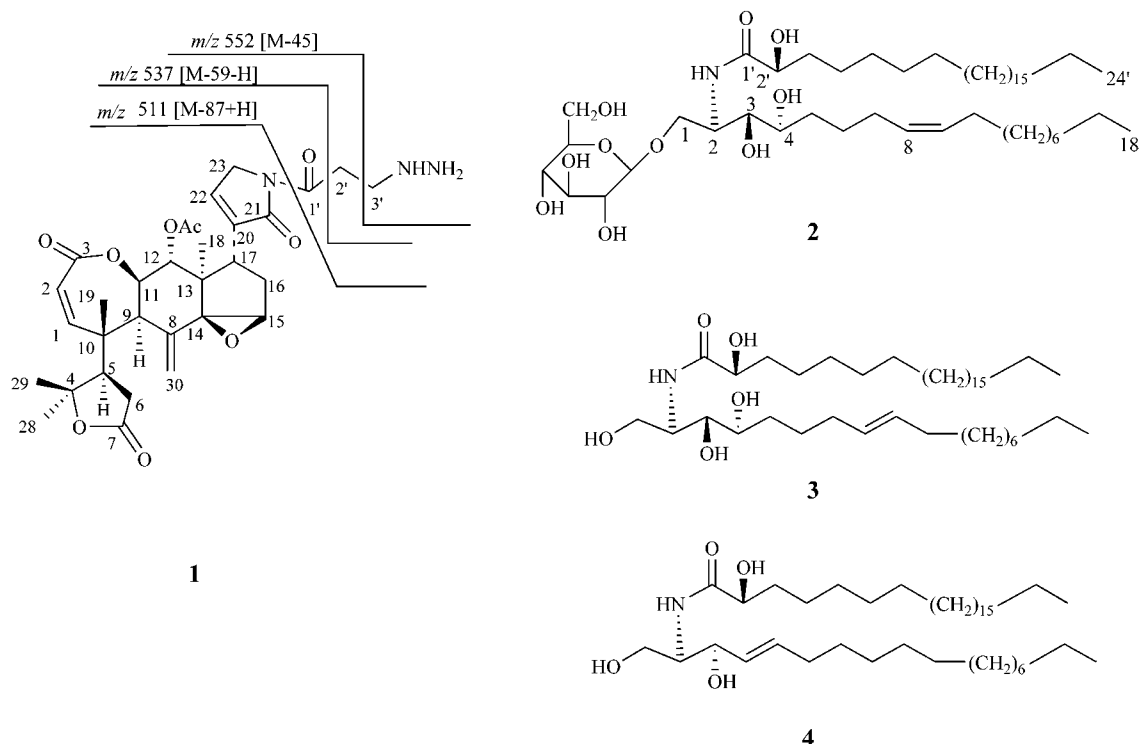


Figure 1. Structures of compounds 1–4.

observation of cross-peaks between  $\delta_C$  170.6 (s,  $\text{CH}_3\text{COO}$ ) and  $\delta_H$  6.47 (1H, d,  $J = 10.8$  Hz, H-12) and  $\delta_H$  1.96 (3H, s,  $\text{CH}_3\text{-COO}$ ), respectively, in the HMBC spectrum. In the  $^1\text{H}$ – $^1\text{H}$  COSY spectrum, the correlation between H-12 and  $\delta_H$  4.93 (1H, dd,  $J = 10.8, 8.1$  Hz) was assigned to H-11. H-11 showed correlations with H-12 and  $\delta_H$  3.78 (1H, d,  $J = 8.1$  Hz), which was assigned H-9. The assignment was further supported by the HMBC spectrum (Table 1). In the NOESY spectrum, NOE interactions between H-12 and H-17 and between H-12 and H-19 placed the acetyl at the  $12\alpha$ -position, whereas NOE interactions between H-11 and H-18 and between H-11 and H-9 suggested an  $11\beta$ -substituent.

The carbon signals at  $\delta_C$  125.0 (d), 148.2 (d), and 167.8 (s) in the  $^{13}\text{C}$  NMR spectrum of **1** and corresponding proton signals at  $\delta_H$  6.56 (1H, d,  $J = 11.7$  Hz) and 6.54 (1H, d,  $J = 11.7$  Hz) in the  $^1\text{H}$  NMR spectrum were typical signals for an  $\alpha,\beta$ -unsaturated lactone moiety in the A ring (15, 23, 25). These doublet signals were assigned to H-1 and H-2, respectively. In the HMBC spectrum, the correlations of  $\delta_C$  167.8 (s) with H-11, H-1, and H-2, respectively, allowed the assignment of  $\delta_C$  167.8 (s, C-3) and indicated a seven-membered ring lactone between C-3 and C-11 in compound **1**. The signal at  $\delta_C$  86.5 (s) was attributed to C-4 because the HMBC spectrum showed correlations of  $\delta_C$  86.5 (s) with  $\delta_H$  1.34 (3H, s, H-28) and 1.37 (3H, s, H-29). The B ring has been cleaved to form a  $\gamma$ -lactone between C-7 and C-4 on the basis of the observation of a weak cross-peak between H-29 and  $\delta_C$  174.4 (s, C-7) in the HMBC spectrum. NOE correlations of H-5 with H-28 and of H-19 with H-29 indicated their *cis*-relationships.

In the HMBC spectrum, the correlations of  $\delta_H$  3.14 (1H, dd,  $J = 10.6, 7.3$  Hz, H-17) with  $\delta_C$  136.9 (s), 170.9 (s), and 139.5 (d), and of  $\delta_H$  6.74 (1H, s) with  $\delta_C$  136.9 (s), 170.9 (s), and 50.9 (t) suggested that these signals [ $\delta_C$  136.9 (s), 170.9 (s), 139.5 (d), and 50.9 (t)] as a unit were attached to C-17. On the basis of a comparison of the  $^{13}\text{C}$  NMR spectral data with those of tetranortriterpenoids in the literature carrying a 23-hydroxy-20(22)-ene-21,23- $\gamma$ -lactone unit (23, 24, 26), a 20(22)-ene-

21,23- $\gamma$ -lactone mimic unit attached to C-17 in **1** [ $\delta_C$  136.9 (s, C-20), 170.9 (s, C-21), 139.5 (d, C-22), and 50.9 (t, C-23)] was proposed. C-23 was shifted upfield  $\sim 20$  ppm compared to normal oxymethylene. The data suggest a 20(22)-ene-21,23- $\gamma$ -lactam unit rather than a 20(22)-ene-21,23- $\gamma$ -lactone unit attached to C-17 in **1**, which is consistent with the molecular formula of the compound. The HMBC spectrum showing correlations of  $\delta_H$  3.86 and 3.78 (each 1H, s, H-23) with C-20, C-21, C-22, and C-1' [ $\delta_C$  175.3 (s)] and its molecular formula supported the inference and suggested a substituent with two nitrogen atoms attached to the skeleton nitrogen.

The HMBC spectrum showing correlations of  $\delta_H$  2.48 and 2.02 (each 1 H, m, H-2') with  $\delta_C$  175.3 (s, C-1') and 42.0 (t, C-3') and of  $\delta_H$  3.57 (2H, m, H-3') with  $\delta_C$  24.6 (t, C-2') and 175.3 (s, C-1') and the  $^1\text{H}$ – $^1\text{H}$  COSY spectrum with a correlation of  $\delta_H$  2.48 (1H, m, H-2') with  $\delta_H$  3.57 (2H, m, H-3') indicated a  $-\text{CH}_2\text{CH}_2-$  moiety attached to C-1'. The mass fragments at  $m/z$  522 [ $M - 45$ ], 537 [ $M - 59 - \text{H}$ ], and 511 [ $M - 87 + \text{H}$ ] in the EIMS suggested the loss of  $-\text{CH}_2\text{NHNH}_2$ ,  $-\text{CH}_3\text{CH}_2\text{NHNH}_2$ , and  $-\text{COCH}_2\text{CH}_2\text{NHNH}_2$  fragments, respectively. The correlation of  $\delta_H$  2.47 (1H, m, NH) with  $\delta_C$  42.0 (t, C-3') and 24.6 (t, C-2') in the HMBC spectrum and the correlation of  $\delta_H$  2.47 (1H, m, NH) with  $\delta_H$  2.00 (2H, m,  $\text{NH}_2$ ) in the  $^1\text{H}$ – $^1\text{H}$  COSY spectrum supported the existence of a  $-\text{COCH}_2\text{CH}_2\text{NHNH}_2$  substituting group linked to the nitrogen. On the basis of the above evidence, the structure of **1** was elucidated as shown (Figure 1), named munroniamide. All signals were assigned in Table 1 on the basis of an analysis of 2D NMR data. The side chain of **1**, which was similar to ceramide derivatives, was unprecedented in tetranortriterpenoids.

Meanwhile, three ceramides (**2**–**4**) co-occurred in *M. henryi*. Their structures were identified by comparison with literature values (19–21). Ceramides are distributed ubiquitously in the members of eukaryotic cells (27), where they were previously thought to play a structural role. Marine organisms are a rich source of ceramides. Ceramides have also been isolated from plants, fungi, insects, and human skin (28–31). To our

**Table 2.** Antifeedant Activity of Compounds 1–4 Bioassayed with *P. brassicae* L.

compound	AR <sup>a</sup> (100%)	mortality (100%)
munroniamide (1)	27.6	10
1- <i>O</i> -β-D-glucopyranosyl-(2 <i>S</i> ,3 <i>S</i> ,4 <i>R</i> ,8 <i>Z</i> )-2- <i>N</i> -(2'-hydroxytetraacosanoyl)heptadecaspingha-8-ene (2)	62.0	50
(2 <i>S</i> ,3 <i>S</i> ,4 <i>R</i> ,8 <i>E</i> )-2- <i>N</i> -(2'-hydroxytetraacosanoyl)-heptadecaspingha-8-ene (3)	3.0	0
(2 <i>S</i> ,3 <i>R</i> ,4 <i>E</i> )-2- <i>N</i> -(2'-hydroxytetraacosanoyl)-heptadecaspingha-4-ene (4)	0	0
azadirachtin	99.5	100

<sup>a</sup> AR represents the antifeeding rate calculated from  $AR = [(C - T)/C] \times 100\%$ . *C* and *T* represent the areas eaten by the larvae of the control and treatment disks, respectively.

knowledge, no ceramides have previously been reported from the family Meliaceae, except for a known ceramide from *Cipadessa baccifera* reported by our laboratory.

The antifeedant activities of compounds 1–4 were tested by the conventional leaf disk method against the larvae of *P. brassicae* L. The results indicated that 2 had significant activity by lower than that of the model compound azadirachtin (Table 2).

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#### LITERATURE CITED

- Huang, R. C.; Okamura, H.; Iwagawa, T.; Tadera, K.; Nakatani, M. Azedarachin C, a limonoid antifeedant from *Melia azedarach*. *Phytochemistry* **1995**, *38*, 593–594.
- Nakani, M.; Arikawa, S.; Okamura, H.; Iwagawa, T. Isolation of a new insect antifeeding azadirachtin derivative from Okinawan *Melia azedarach* Linn. *Heterocycles* **1994**, *38*, 327–331.
- Nakatani, M.; Zhou, J. B.; Nakayama, N.; Okamura, H.; Iwagawa, T. Nimbolidins C–E, limonoid antifeedants from *Melia toosendan*. *Phytochemistry* **1996**, *41*, 739–743.
- Ahn, J. W.; Choi, S. U.; Lee, C. O. Cytotoxic limonoids from *Melia azedarach* var. *Japanica*. *Phytochemistry* **1994**, *36*, 1493–1495.
- Itokawa, H.; Qiao, Z. S.; Hirobe, C.; Takeya, K. Cytotoxic limonoids and tetranortriterpenoids from *Melia azedarach*. *Chem. Pharm. Bull.* **1995**, *43*, 1171–1175.
- Takeya, K.; Qiao, Z. S.; Hirobe, C.; Itokawa, H. Cytotoxic azadirachtin-type limonoids from *Melia azedarach*. *Phytochemistry* **1996**, *42*, 709–712.
- Nakatani, M.; Huang, R. C.; Okamura, H.; Iwagawa, T.; Tadera, K. Degraded limonoids from *Melia azedarach*. *Phytochemistry* **1998**, *49*, 1773–1776.
- Segura-Correa, R.; Mata, R.; Anaya, A. L.; Hernandez-Bautista, B.; Vllena, R.; Soriano-Garcia, M.; Bye, R.; Linares, E. New tetranortriterpenoids from *Swietenia humilis*. *J. Nat. Prod.* **1993**, *56*, 1567–1574.
- Musza, L. L.; Killar, I. M.; Speight, P.; Mcelhiney, S.; Barrow, C. J.; Gillum, A. M.; Cooper, R. Potent new cell adhesion inhibitory compounds from the root of *Trichilia rubra*. *Tetrahedron* **1994**, *50*, 11369–11378.
- Musza, L. M.; Killar, L. M.; Speight, P.; Barrow, C. J.; Gillum, A. M.; Cooper, R. Minor limonoids from *Trichilia rubra*. *Phytochemistry* **1995**, *39*, 621–624.

- Jimenez, A.; Villarreal, C.; Toscano, R.; Cook, M.; Arnason, J. T.; Bye, R.; Mata, R. Limonoids from *Swietenia humilis* and *Guarea grandiflora* (Meliaceae). *Phytochemistry* **1998**, *49*, 1981–1988.
- Yunnan Institute of Botany. *Munronia Wight: M. henryi* Harms. In *Flora Yunnanica*; Science Press: Beijing, China, 1977; Vol. 1, pp 214–216.
- Luo, X. D.; Wu, S. H.; Ma, Y. B.; Wu, D. G. Components of *Cipadessa baccifera*. *Phytochemistry* **2000**, *55*, 867–872.
- Luo, X. D.; Wu, S. H.; Ma, Y. B.; Wu, D. G. Tetranortriterpenoids from *Walsura yunnanensis*. *J. Nat. Prod.* **2000**, *63*, 947–951.
- Luo, X. D.; Wu, S. H.; Ma, Y. B.; Wu, D. G. Prieurianin-type tetranortriterpenoids from the bark of *Dysoxylum hainanense*. *Heterocycles* **2000**, *53*, 2225–2232.
- Luo, X. D.; Ma, Y. B.; Wu, S. H.; Wu, D. G. Two novel azadirachtin derivatives from *Azadirachta indica*. *J. Nat. Prod.* **1999**, *62*, 1022–1024.
- Luo, X. D.; Wu, S. H.; Wu, D. G.; Ma, Y. B.; Qi, S. H. Novel antifeeding limonoids from *Dysoxylum hainanense*. *Tetrahedron* **2002**, *58*, 7797–7804.
- Luo, X. D.; Wu, S. H.; Ma, Y. B.; Wu, D. G. Limonoids and phytol derivatives from *Toona sinensis*. *Fitoterapia* **2000**, *71*, 492–496.
- Sam, S. K.; Ju, S. K.; Kun, H. S.; Hyun, P. K.; Hyeun, W. C. Cyclooxygenase-2 inhibitory cerebroside from *Phytolacca radix*. *Chem. Pharm. Bull.* **2001**, *49*, 321–323.
- Hua, H. M.; Cheng, M. S.; Li, X. The structure identification of ceramide constituent from *Linaria vulgaris*. *Chinese J. Med. Chem.* **2000**, *10*, 57–59.
- Mendelsohn, R.; Rerek, M. E.; Moore, D. J. Infrared spectroscopy and microscopic imaging of stratum corneum models and skin. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4651–4657.
- Adul, G. O.; Bentley, M. D.; Benson, B. W.; Huang, F. Y.; Gelbaum, L.; Hassanali, A. Two new prieurianin-class limonoids from *Turraea mombasana*. *J. Nat. Prod.* **1993**, *56*, 1414–1417.
- Garcez, F. R.; Garcez, W. S.; Tsutsumi, M. T.; Roque, N. F. Limonoids from *Trichilia elegans* ssp. *Elegans*. *Phytochemistry* **1997**, *45*, 141–148.
- Lydia, R. H.; Jorge, C.; Carlos, A. Trichavensin, a prieurianin derivative from *Trichilia havanensis*. *Phytochemistry* **1996**, *43*, 457–459.
- Okorie, D. A. Chromones and limonoids from *Harrisonia abyssinica*. *Phytochemistry* **1982**, *21*, 2424.
- Siddiqui, S.; Mahmood, T.; Faizi, S.; Siddiqui, B. S. Studies in the chemical constituents of *Azadirachta indica* A. Juss (Meliaceae). Part 10. Isolation and structure elucidation of isonimolcinolide, the first 17-acetoxy tetranortriterpenoid and nimolcinic acid, the first hexanortriterpenoid with an apoeuphane (apotirucallane) skeleton. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1429–1432.
- Sweeley, C. C. In *Biochemistry of Lipids, Lipoproteins, and Membranes*; Vance, D. E., Vance, J. E., Eds.; Elsevier: Amsterdam, The Netherlands, 1991; pp 327–361.
- Kim, S. Y.; Choi, Y. H.; Huh, H.; Kim, J.; Kim, Y. H.; Lee, H. S. *J. Nat. Prod.* **1997**, *60*, 274–276.
- Qi, J.-H.; Ojika, M.; Sakagami, Y. *Tetrahedron* **2000**, *56*, 5835–5841.
- Dennis, R. D.; Deyer, R.; Egge, H.; Menges, H.; Stirn, S.; Wiegandt, H. *Eur. J. Biochem.* **1985**, *146*, 51–58.
- Robson, K. J.; Stewart, M. E.; Michelsen, S.; Lazo, N. D.; Downing, D. J. *Lipids Res.* **1994**, *35*, 2060–2068.

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