Natural Product Sciences
19(4) : 342-346 (2013)

A New Apotirucallane-type Triterpenoid from the Fruit of *Melia azedarach*

Qinghao Jin[1], Chul Lee[1], Jin Woo Lee[1], Moon-Soon Lee[2], Mi Kyeong Lee[1], and Bang Yeon Hwang[1,*]

[1]*College of Pharmacy, Chungbuk National University, Cheongju 361-763, Korea*
[2]*College of Agriculture, Life and Environmental Sciences, Chungbuk National University, Cheongju 361-763, Korea*

Abstract – A new apotirucallane-type triterpenoid, 3α-tigloylsapelin D (**1**) together with five known triterpenoids such as meliasenin B (**2**), sendanolactone (**3**), (−)-12β-hydroxykulactone (**4**), cinamodiol (**5**), and 3α-hydroxytirucalla-7,24(25)-dien-6-oxo-21,16-olide (**6**) were isolated from the fruits of *Melia azedarach*. Their structures were established on the basis of various NMR spectroscopic analyses including 2D-NMR techniques (HSQC, HMBC, and NOESY) and HR-FAB-MS data.
Keywords – *Melia azedarach*, Meliaceae, Apotirucallane-type triterpenoid

Introduction

Melia azedarach L. (Meliaceae) is a deciduous tree which is native to Persia, India, and China, and distributed widely in China, Japan, and Southeast Asia. The dried stem bark, root bark, and fruit of this plant have been used as anthelmintic, antifeedant, and for the treatment of leprosy, eczema, asthma, malaria, fever, cholelithiasis, acariasis, and pain (Tang and Eisenbrand, 2011; Jung and Shin, 1990). Previous phytochemical studies on this plant have afforded a wide range of compounds including limonoid, triterpenoid, steroid, alkaloid, and flavonoid glycosides (Zhao *et al.*, 2010). *M. azedarach* and limonoids have attracted considerable interest because of their biological activivities, including antioxidant, anticancer, antimicrobial, antifeedant, insecticidal, antifungal, anti-inflammatory, and analgesic effects (Tan and Luo, 2011; Marimuthu *et al.*, 2013; Kim *et al.*, 1994; Akihisa *et al.*, 2013; Liu *et al.*, 2011; Carpinella *et al.*, 2003a, 2003b; Xie *et al.*, 2008).

We investigated the chemical constituents of the fruits of this plant and found a new apotirucallane-type triterpenoid along with five known compounds. The structure of the new compound was elucidated by means of spectroscopic methods including 2D NMR techniques and mass spectrometry to be named as 3α-tigloylsapelin D (**1**).

*Author for correspondence
Bang Yeon Hwang, College of Pharmacy, Chungbuk National University, Cheongju 361-763, Korea
Tel: +82-43-261-2814; E-mail: byhwang@chungbuk.ac.kr

Experimental

General Experimental Procedures – Optical rotations were determined on JASCO DIP-370 polarimeter at 25 °C. NMR spectra were obtained using a Bruker AMX-500 MHz NMR spectrometer. HR-FAB-MS and ESI-MS spectra were obtained on JMS 700 (JEOL, Tokyo, Japan) and VG Autospec Ultima (Micromass, Manchester, UK) mass spectrometers, respectively. Open column chromatography was performed using a silica gel 60 (Kiesel gel 60, 700 - 230 and 230 - 400 mesh, Merck). Preparative HPLC was carried out on a Waters system (two 515 pumps and a 2996 photodiode array detector) and a YMC J'sphere ODS-H80 column (4 μm, 150 × 20 mm), using the mixed solvent system CH_3CN/H_2O at a flow rate of 6.0 mL/min. Thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} (0.25 mm, Merck). All other chemicals and reagents were analytical grade.

Plant Material – The dried fruits of *M. azedarach* were purchased from Kyung-dong market, Seoul, Korea, in October 2010. The voucher specimen (CBNU 2010-003) was identified by Emeritus Professor Kyong Soon Lee and deposited at the Herbarium of College of Pharmacy, Chungbuk National University.

Extraction and Isolation – The dried fruits (1.0 kg) were extracted three times with methanol (3 × 2 L) at room temperature. The solvent was removed at reduced pressure to give a brown residue (179 g). The extract was suspended in H_2O (1 L), and separated with *n*-hexane (3 × 1 L), CH_2Cl_2 (3 × 1 L), and EtOAc (3 × 1 L), respectively. The CH_2Cl_2 extract (12 g) was then subjected to column chromatography over silica gel (column: 20 cm × 7.0 cm)

with CH_2Cl_2 - MeOH gradient (100 : 0 - 0 : 100) to yield 7 fractions (MA1 - MA7). Following silica gel column chromatography of MA4 fraction with a solvent gradient of EtOAc in *n*-hexane yielded 6 subfractions (MA4-1 - MA4-6). Among them, MA4-1 fraction yielded compound **1** (2.6 mg) by an additional purification step on the RP-HPLC (MeCN : H_2O gradient from 85 : 15 to 100 : 0). And then, compound **2** (3.0 mg) was isolated by RP-HPLC (MeCN : H_2O = 75 : 25, isocratic) from AM4-4 fraction. Following silica gel column chromatography of MA3 fraction with a solvent gradient of ethyl acetate in *n*-hexane yielded 6 subfractions (MA3-1-MA3-6). Compounds **3** (4.5 mg) and **4** (2.5 mg) were isolated from MA3-2-1 fraction by RP-HPLC (MeCN : H_2O = 80 : 20, isocratic). The MA3-3-5 fraction was further separated on RP-HPLC (MeCN : H_2O gradient from 60 : 40 to 80 : 20) to give compounds **5** (4.0 mg) and **6** (2.0 mg).

3α-Tigloylsapelin D (1) – Amorphous powder; α_D^{25} : –49 (*c* 0.05, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$); see Table 1; HR-FBA-MS *m/z* 595.3977 $[M + Na]^+$ (calcd for $C_{35}H_{56}O_6Na$, 595.3975).

Meliasenin B (2) – White solid; α_D^{25} : –28 (*c* 0.1, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): δ 5.69 (1H, br d, *J* = 2.5 Hz, H-7), 5.17 (1H, t, *J* = 7.0 Hz, H-24), 4.31 (1H, td, *J* = 10.5, 7.5 Hz, H-16), 3.21 (1H, t, *J* = 8.0 Hz, H-3), 3.10 (1H, td, *J* = 10.0, 3.5 Hz, H-9), 1.72 (3H, s, H-27), 1.66 (3H, s, H-26), 1.33 (3H, s, H-29), 1.29 (3H, s, H-30), 1.09 (3H, s, H-18), 1.05 (3H, s, H-29), 0.90 (3H, s, 19); ^{13}C-NMR (125 MHz, CD_3OD): δ 200.8 (6), 181.0 (C-21), 169.4 (C-8), 132.1 (C-25), 123.7 (C-7), 123.3 (C-24), 81.7 (C-16), 78.0 (C-3), 65.5 (C-5), 57.4 (C-17), 55.9 (C-14), 49.7 (C-9), 44.9 (C-20), 44.3 (C-10), 39.2 (C-13), 37.8 (C-4), 36.3 (C-1), 34.4 (C-15), 28.8 (C-22), 28.8 (C-12), 28.8 (C-30), 27.5 (C-28), 26.0 (C-2), 25.6 (C-23), 24.4 (C-26), 20.1 (C-18), 16.5 (C-27), 16.1 (C-11), 14.1 (C-29), 12.9 (C-19). ESI-MS *m/z* 491.43 $[M + Na]^+$.

Sendanolactone (3) – White solid; α_D^{25} : –35 (*c* 0.1, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): δ 5.78 (1H, br d, *J* = 2.5 Hz, H-7), 5.17 (1H, t, *J* = 7.5 Hz, H-24), 4.30 (1H, td, *J* = 11.5, 8.0 Hz, H-16 Hz), 1.72 (3H, s, H-27), 1.66 (3H, s, H-26), 1.37, 1.36, 1.34, 1.15, 1.05 (15H, s, H-18, 19, 28, 29, 30 each); ^{13}C-NMR (125 MHz, CD_3OD): δ 215.5 (C-3), 199.1 (C-6), 180.8 (C-21), 169.8 (C-8), 132.1 (C-25), 123.5 (C-7), 123.3 (C-24), 81.6 (C-16), 64.9 (C-5), 57.3 (C-17), 55.9 (C-14), 48.6 (C-9), 48.2 (C-4), 46.7 (C-20), 44.8 (C-10), 39.1 (C-13), 36.4 (C-1), 34.3 (C-15), 33.5 (C-2), 28.8 (C-30), 28.7 (C-22), 28.6 (C-12), 25.6 (C-23), 24.4 (C-27), 24.3 (C-28), 20.7 (C-29), 19.9 (C-18), 16.5 (C-26), 16.1 (C-11), 12.4 (C-19). ESI-MS *m/z* 489.50 $[M + Na]^+$.

(–)-12β-Hydroxykulactone (4) – Colorless oil; α_D^{25} : –24 (*c* 0.1, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): δ 5.41 (1H, br s, H-7), 5.14 (1H, t, *J* = 7.0 Hz, H-24), 4.26 (1H, dd, *J* = 18.0, 10.0 Hz, H-16α), 3.98 (1H, dd, *J* = 9.5, 5.0 Hz, H-12α), 2.85 (1H, td, *J* = 14.5, 5.0 Hz, H-9), 1.69 (3H, s, H-27), 1.65 (3H, s, H-26), 1.41 (3H, s, H-30), 1.15 (3H, s, 28), 1.08 (3H, s, H-29), 1.04 (3H, s, H-19), 0.87 (3H, s, H-18); ^{13}C-NMR (125 MHz, CD_3OD): δ 217.7 (C-3), 182.0 (C-21), 143.6 (C-8), 131.8 (C-25), 123.9 (C-24), 118.5 (C-7), 82.5 (C-16), 70.8 (C-12), 54.7 (C-13), 53.1 (C-17), 52.4 (C-5), 48.4 (C-4), 48.3 (C-9), 45.3 (C-20), 44.0 (C-14), 38.1 (C-1), 36.0 (C-15), 35.1 (C-10), 34.4 (C-2), 33.3 (C-30), 30.1 (C-11), 28.4 (C-22), 25.4 (C-23), 24.7 (C-26), 24.1 (C-6), 23.7 (C-29), 20.7 (C-28), 19.3 (C-18), 16.9 (C-27), 11.7 (C-19). ESI-MS *m/z* 491.25 $[M + Na]^+$.

Cinamodiol (5) – White solid; α_D^{25} : –34 (*c* 0.125, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): δ 5.37(1H, m, H-7), 5.16 (1H, br td, *J* = 6.8 Hz, H-24), 4.28 (1H, dd, *J* = 17.5, 9.5 Hz, H-16α), 3.96 (1H, dd, *J* = 9.5, 5.0 Hz, H-12α), 3.20 (1H, dd, *J* = 10.0, 6.0 Hz, H-3α), 1.71 (3H, s, H-27), 1.66 (3H, s, H-26), 1.37 (3H, s, H-30), 0.97 (3H, s, H-29), 0.88 (3H, s, H-19), 0.87 (3H, s, H-28), 0.82 (3H, s, H-18), ^{13}C-NMR (125 MHz, CD_3OD): δ 181.9 (C-21), 143.4 (C-8), 131.6 (C-25), 124.0 (C-24), 118.6 (C-7), 82.4 (C-16), 78.3 (C-3), 70.9 (C-12), 54.6 (C-14), 53.0 (C-17), 50.8 (C-5), 48.5 (C-9), 45.2 (C-20), 44.0 (C-13), 38.6 (C-4), 36.9 (C-1), 35.8 (C-15), 34.9 (C-10), 33.0 (C-30), 30.1 (C-22), 28.4 (C-11), 26.9 (C-2), 26.7 (C-28), 25.3 (C-27), 24.5 (C-23), 24.9 (C-6), 19.0 (C-19), 16.6 (C-26), 13.8 (C-29), 12.0 (C-18). ESI-MS *m/z* 493.33 $[M + Na]^+$.

3α-Hydroxytirucalla-7,24(25)-dien-6-oxo-21,16-olide (6) – White solid; α_D^{25} : –42 (*c* 0.1, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): δ 5.69 (1H, br d, *J* = 2.5 Hz, H-7), 5.17 (1H, br dt, *J* = 6.0 Hz, H-24), 4.31 (1H, dt, *J* = 10.5, 7.5 Hz, H-16α), 3.29 (1H, br s, H-3α), 3.20 (1H, dt, *J* = 8.0, 2.0 Hz, H-9), 1.72 (3H, s, H-27), 1.67 (3H, s, H-26), 1.34 (3H, s, H-28), 1.23 (3H, s, H-28), 1.14 (3H, s, H- 29), 1.07 (3H, s, H-18), 0.92 (3H, s, H-19); ^{13}C-NMR (125 MHz, CD_3OD): δ 202.2 (C-6), 181.1 (C-21), 169.5 (C-8), 132.1 (C-25), 123.7 (C-7), 123.3 (C-24), 81.7 (C-16), 76.0 (C-3), 60.5 (C-5), 57.4 (C-17), 55.9 (C-14), 49.7 (C-9), 44.8 (C-20), 44.1 (C-10), 39.1 (C-13), 36.4 (C-4), 34.4 (C-15), 30.6 (C-1), 28.8 (C-22), 28.8 (C-12), 28.8 (C-30), 27.3 (C-28), 25.6 (C-23), 24.4 (C-27), 24.2 (C-2), 20.7 (C-29), 20.1 (C-18), 16.5 (C-26), 16.0 (C-11), 13.1 (C-19). ESI-MS *m/z* 491.33 $[M + Na]^+$.

Results and Discussion

The CH_2Cl_2-soluble fraction of the dried fruits of *M.*

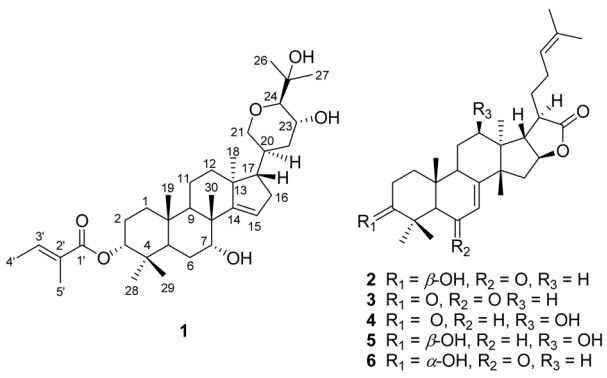

Fig. 1. The structures of compounds **1 - 6** isolated from *M. azedarach*.

azedarach was subjected to silica gel column chromatography and preparative RP-HPLC which led to the isolation of six compounds including a new apotirucallane-type triterpenoid, 3α-tigloylsapelin D (**1**) (Fig. 1). Among these compounds, five known compounds were identified as meliasenin B (**2**) (Zhang *et al.*, 2010), sendanolactone (**3**) (Faizi *et al.*, 2002; Ochi *et al.*, 1977), (−)-12β-hydroxykulactone (**4**) (Cantrell *et al.*, 1999), cinamodiol (**5**) (Kelecom *et al.*, 1996), and 3α-hydroxytirucalla-7,24(25)-dien-6-oxo-21,16-olide (**6**) (Tan *et al.*, 2010) by comparing the ^{1}H-HMR, ^{13}C-NMR and MS spectroscopic data with those in the literature.

Compound **1** was isolated as white amorphous powder. The HR-FAB-MS showed the quasi-molecular ion peak at *m/z* 595.3977 $[M + Na]^+$ (calcd for $C_{35}H_{56}O_6Na$, 595.3975), consistent with the molecular formula of $C_{35}H_{56}O_6$. The ^{1}H-NMR spectrum (Table 1) showed seven tertiary methyl groups (δ_H 0.89, 0.93, 0.94, 1.02, 1.11, each 3H, s), one olefinic proton (δ_H 5.52), and five oxygenated protons (δ_H 3.46, 3.90, 3.93, 4.01, 4.71). The ^{13}C-NMR spectra (Table 1) showed the presences of seven methyls, eight methylenes (one oxygenated), nine methines (three oxygenated, one olefinic), and six quaternary carbons (one olefinic and one oxygenated). The remaining ^{1}H-NMR and ^{13}C-NMR data (Table 1) indicated the presence of a tigloyl group [δ_H 6.88 (1H, dd, 7.0, 1.5 Hz, H-3'), 1.87 (3H, t, 1.0 Hz, H-4'), and 1.81 (3H, dd, 7.0, 1.0 Hz, H-5'); δ_C 167.6, 136.7, 129.2, 14.4, 12.1]. The aforementioned data suggested that compound **1** was a triterpenoid having an apotirucallane skeleton with a tigloyl ester group in the molecule. Moreover, these data closely resembled to those of sapelin D and 3α-senecioyl-21,24*R*-epoxyapotirucall-14-ene-7α,23*R*,25-triol, apotirucallane-type triterpenoid from *Entandrophragma cylindricurn* and *Cedrela sinensis*, respectively (Lyons and Taylor, 1976; Mitsui *et al.*, 2005, 2007). The location of tigloyl group was elucidated as C-3 by the observed HMBC correlation between H-3 (δ_H 4.71) and C-1' (δ_C 167.6) (Fig. 2). In the HMBC spectrum of compound **1**, the correlations between the methylene protons [δ_H 3.46 (1H, dd, 11.0, 2.5 Hz, H-21α) and δ_H

Table 1. ^{1}H- (500 MHz) and ^{13}C-NMR (125 MHz) data of compound **1** (in $CDCl_3$)[a]

Carbon	**1**	
No.	δ_H	δ_C
1	1.52 (2H, m)	33.5
2	1.75 (2H, m)	22.7
3	4.71(1H, t, 2.5)	77.5
4	–	36.3
5	2.09 (1H, m)	41.8
6	1.68 (2H, m)	23.7
7	3.93 (1H, t, 2.5)	72.3
8	–	44.5
9	2.02 (1H, m)	41.8
10	–	37.5
11	1.64 (2H, m)	16.4
12	1.52 (2H, m)	34.2
13	–	46.7
14	–	162.3
15	5.52 (1H, br d, 2.5)	119.8
16(α)	2.38(1H, ddd, 15.0, 7.0, 3.5)	34.9
16(β)	2.08 (1H, m)	
17	2.04 (1H, m)	52.2
18	1.02 (3H, s)	19.2
19	0.93 (3H, s)	15.3
20	2.04 (1H, m)	35.8
21(α)	3.46 (1H, dd, 11.0, 2.5)	70.1
21(β)	4.01 (1H, d, 11.0)	
22(α)	1.55 (1H, m)	36.4
22(β)	2.03 (1H, m)	
23	3.90 (1H, m)	64.4
24	2.92 (1H, d, 9.0)	86.5
25	–	74.2
26	1.30 (3H, s)	24.0
27	1.34 (3H, s)	28.6
28	0.89 (3H, s)	27.8
29	0.94 (3H, s)	21.7
30	1.11 (3H, s)	27.8
1'	–	167.6
2'	–	136.7
3'	6.88 (1H, dd, 7.0, 1.5)	129.2
4'	1.87 (3H, t, 1.0)	12.1
5'	1.81 (3H, dd, 7.0, 1.0)	14.4

[a] Assignments were confirmed by HMQC, HMBC and NOESY spectra.

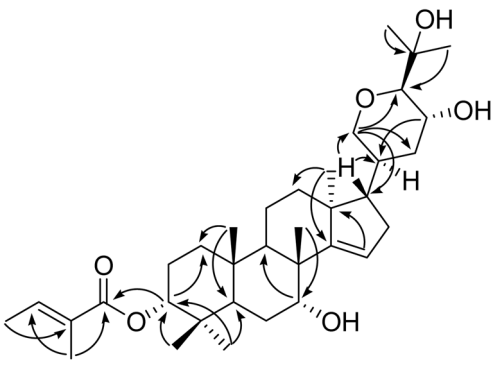

Fig. 2. Key HMBC (→) correlations of compound **1**.

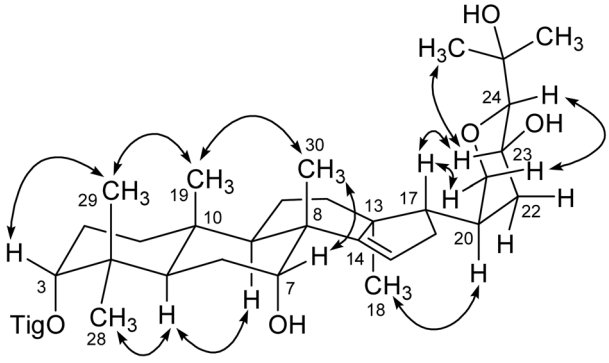

Fig. 3. Key NOESY (↔) correlations of compound **1**.

4.01 (1H, d, 11.0 Hz, H-21β)] and the methine carbon [δ_C 86.5 (C-24)] suggested that C-21 was linked to C-24 via an oxygen bridge to form a cyclic ether (Fig. 2). The relative configuration of the tetracyclic core in compound **1** was established on the basis of NOESY experiments (Fig. 3). The NOESY correlations of H-3β/CH_3-29, CH_3-19/CH_3-29, CH_3-19/CH_3-30, and CH_3-30/H-7 indicated the tigloyl ester side chain at C-3 and hydroxyl group at C-7 were both in α-orientation. The large coupling constant (J = 9.0 Hz) between H-23 and H-24 indicated that the tetrahydropyran ring of the side chain at C-17 was in a chair conformation (Mitsui *et al.*, 2005; Zhang *et al.*, 2012). Further NOE correlations between H-17/H-21β, H-17/H-23, CH_3-18/H-20, H-20/H-21α, H-21α/H-22α, H-21α/H-24, and H-22α/H-24 revealed that the configuration at C-23 and that at C-24 were both *R*. Therefore, the structure of **1** was determined as 3α-tigloyl-21,24*R*-epoxyapotirucall-14-ene-7α,23*R*,25-triol, and named 3α-tigloylsapelin D (**1**).

The genus *Melia* is well-known as a rich and valuable source of highly functionalized nortriterpenoid such as limonoid derivatives (Tan and Luo, 2011). Apotirucallane-type triterpenoids, which have undergone the apo-euphol rearrangement to form a C = C bond at C-14 with the methyl group shifted to C-8, were isolated from the genus *Melia* (Zhao *et al.*, 2010; Mitsui *et al.*, 2005; Nakanishi *et al.*, 1986; Zeng *et al.*, 1995a; Rogers *et al.*, 1998; Fukuyama *et al.*, 2000).

However, apotirucallane-type triterpenoids having a substituted tetrahydropyran ring side chain have been rarely found (Zeng *et al.*, 1995b, 1995c). Therefore, the isolation of 3α-tigloylsapelin D (**1**) in this study provides further example of the rare apotirucallae-type triterpenoid with tetrahydropyran ring system in the molecule.

Acknowledgements

This work was supported by the research grant of the Chungbuk National University in 2011.

References

Akihisa, T., Pan, X., Nakamura, Y., Kikuchi, T., Takahashi, N., Matsumoto, M., Ogihara, E., Fukatsu, M., Koike, K., and Tokuda, H., Limonoids from the fruits of *Melia azedarach* and their cytotoxic activities. *Phytochemistry* **89**, 59-70 (2013).

Cantrell, C.L., Rajab, M.S., Franzblau, S.G., and Fischer, N.H., Antimycobacterial triterpenes from *Melia volkensii*. *J. Nat. Prod.* **62**, 546-548 (1999).

Carpinella, M.C., Defago, M.T., Valladares, G., and Palacios, S.M., Antifeedant and insecticide properties of a limonoid from *Melia azedarach* (Meliaceae) with potential use for pest management. *J. Agric. Food Chem.* **51**, 369-374 (2003a).

Carpinella, M.C., Giorda, L.M., Ferrayoli, C.G., and Palacios, S.M., Antifungal effects of different organic extracts from *Melia azedarach* L. on phytopathogenic fungi and their isolated active components. *J. Agric. Food Chem.* **51**, 2506-2511 (2003b).

Faizi, S., Wasi, A., Siddiqui, B.S., and Naz, A., New terpenoids from the roots of *Melia azedarach*. *Aust. J. Chem.* **55**, 291-296 (2002).

Fukuyama, Y., Ogawa, M., Takahashi, H., and Minami, H., Two new meliacarpinins from the roots of *Melia azedarach*. *Chem. Pharm. Bull.* **48**, 301-303 (2000).

Jung, B.S. and Shin, M.K., *Encyclopedia of Illustrated Korean Natural Drugs*, Young Lim Sa, Seoul, p. 773 (1990).

Kelecom, A., Cabral, M.M.O., and Garcia, E.S., A new euphane triterpene from the Brazilian *Melia azedarach*. *J. Braz. Chem. Soc.* **7**, 39-41 (1996).

Kim, H.M., Oh, G.T., Han, S.B., Hong, D.H., Hwang, B.Y., Kim, Y.H., and Lee, J.J., Comparative studies of adriamycin and 28-deacetyl sendanin on in vitro growth inhibition of human cancer cell lines. *Arch. Pharm. Res.* **17**, 100-103 (1994).

Liu, H.B., Zhang, C.R., Dong, S.H., Dong, L., Wu, Y., and Yue, J.M., Limonoids and triterpenoids from the seeds of *Melia azedarach*. *Chem. Pharm. Bull.* **59**, 1003-1007 (2011).

Lyons, C.W. and Taylor, D.R., Stereochemistry of sapelin B; correlation with sapelin D. Anomalies in the use of shift reagents for determining the absolute configurations of a-glycols. *J. Chem. Soc. Chem. Commun.* **16**, 647-648 (1976).

Marimuthu, S., Balakrishnan, P., and Nair, S., Phytochemical investigation and radical scavenging activities of *Melia azedarach* and its DNA protective effect in cultured lymphocytes. *Pharm. Biol.* **51**, 1331-1340

(2013).
Mitsui, K., Maejima, M., Saito, H., Fukaya, H., Hitotsuyanagi, Y., and Takeya, K., Triterpenoids from *Cedrela sinensis*. *Tetrahedron* **61**, 10569-10582 (2005).
Mitsui, K., Saito, H., Yamamura, R., Fukaya, H., Hitotsuyanagi, Y., and Takeya, K., Apotirucallane and tirucallane triterpenoids from *Cedrela sinensis*. *Chem. Pharm. Bull.* **55**, 1442-1447 (2007).
Nakanishi, T., Inada, A., Nishi, M., Miki, T., Hino, R., and Fujiwara, T., The structure of a new natural apotirucallane-type triterpene and the stereochemistry of the related terpenes. *Chem. Lett.* **15**, 69-72 (1986).
Ochi, M., Kotsuki, H., Tokoroyama, T., and Kubota, T., The structure of sendanolactone, a new triterpenoid from *Melia azedarach* L. var. *japonica* Makino. *Bull. Chem. Soc. Jpn.* **50**, 2499-2500 (1977).
Rogers, L.L., Zeng, L., Kozlowski, J.F., Shimada, H., Alali, F.Q., Johnson, H.A., and McLaughlin, J.L., New bioactive triterpenoids from *Melia volkensii*. *J. Nat. Prod.* **61**, 64-70 (1998).
Tan, Q.G., Li, X.N., Chen, H., Feng, T., Cai, X.H., and Luo, X.D., Sterols and terpenoids from *Melia azedarach*. *J. Nat. Prod.* **73**, 693-697 (2010).
Tan, Q.G. and Luo, X.D., Meliaceous limonoids: chemistry and biological activities. *Chem. Rev.* **111**, 7437-7522 (2011).
Tang, W. and Eisenbrand, G., *Handbook of Chinese Medicinal Plants*, Wiley-VCH, Weinheim, p. 752 (2011).
Xie, F., Zhang, M., Zhang, C.F., Wang, Z.T., Yu, B.Y., and Kou, J.P., Anti-inflammatory and analgesic activities of ethanolic extract and two limonoids from *Melia toosendan* fruit. *J. Ethnopharmacol.* **117**, 463-466 (2008).
Zeng, L., Gu, Z.M., Chang, C.J., Wood, K.V., and McLaughlin, J.L., Meliavolkenin, a new bioactive triterpenoid from *Melia volkensii* (Meliaceae). *Bioorg. Med. Chem.* **3**, 383-390 (1995a).
Zeng, L., Gu, Z.M., Fang, X.P., Fanwick, P.E., Chang, C.J., Smith, D.L., and McLaughlin, J.L., Two new bioactive triterpenoids from *Melia volkensii* (Meliaceae). *Tetrahedron* **51**, 2477-2488 (1995b).
Zeng, L., Gu, Z.M., Chang, C.J., Smith, D.L., and McLaughlin, J.L., A pair of new apotirucallane triterpenes, meliavolkensins A and B, from *Melia volkensii* (Meliaceae). *Bioorg. Med. Chem. Lett.* **5**, 181-184 (1995c).
Zhang, F., Wang, J.S., Gu, Y.C., and Kong, L.Y., Cytotoxic and anti-inflammatory triterpenoids from *Toona ciliata*. *J. Nat. Prod.* **75**, 538-546 (2012).
Zhang, Y., Tang, C.P., Ke, C.Q., Yao, S., and Ye, Y., Limonoids and triterpenoids from the stem bark of *Melia toosendan*. *J. Nat. Prod.* **73**, 664-668 (2010).
Zhao, L., Huo, C.H., Shen, L.R., Yang, Y., Zhang, Q., and Shi, Q.W., Chemical constituents of plants from the genus *Melia*. *Chem. Biodivers.* **7**, 839-859 (2010).

Received September 30, 2013
Revised November 10, 2013
Accepted November 22, 2013