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# A New Tirucallane-Type Triterpenoid Derivative, Lipomelianol from Fruits of *Melia toosendan* SIEB. *et* ZUCC.[1)]

TSUTOMU NAKANISHI,*[,a] AKIRA INADA,[a] and DAVID LAVIE[b]

*Faculty of Pharmaceutical Sciences, Setsunan University,[a] 45–1 Nagaotoge-cho, Hirakata, Osaka 573–01, Japan and Department of Organic Chemistry, The Weizmann Institute of Science,[b] 76100 Rehovot, Israel*

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A new tirucallane-type triterpenoid derivative, which we have named lipomelianol, has been obtained, together with a known triterpenoid, melianone (**4**), from fruits of *Melia toosendan* SIEB. *et* ZUCC. Lipomelianol was established to be a mixture of the 3-*O*-stearate, palmitate, myristate, and laurate (*ca.* 3:35:32:30) of melianol (**3**), as shown by formula **1**, based on chemical, physicochemical, and spectral evidence. High-resolution $^{13}$C-nuclear magnetic resonance data for **1**, **3**, and **4** are also reported.

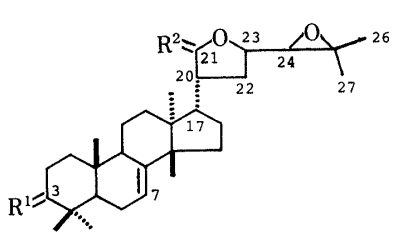
**Keywords**——*Melia toosendan*; Meliaceae; fruit; lipomelianol; melianol; stearic acid; palmitic acid; myristic acid; lauric acid; melianone

The fruit of *Melia toosendan* SIEB. *et* ZUCC.[2)] [*M. azedarach* L. var. *toosendan* (SIEB. *et* ZUCC.) Makino][3)] (Meliaceae) is used as a Chinese crude drug (Chuan-Lian-Zi in Chinese; Sen-Ren-Shi in Japanese) and has so far been used in China as an anodyne for stomach ache due to roundworms, gripe, *etc.*,[2,3a)] and also as a vermicide.[2,3b)] Up to now, a number of limonoids and triterpenoids (tirucallane type, *etc.*) have been characterized from various plants in the family Meliaceae.[4)] However, no report has appeared on the chemical principles from *M. toosendan*, except for the isolation and identification of a limonoid, toosendanin, from the bark.[5)]

In our study on chemical components contained in the fruit of the plant, a new tirucallane-type triterpenoid derivative named lipomelianol[6)] (0.04% from the extr.) has been obtained, together with a known tirucallane-type triterpenoid, melianone (0.30%), from the MeOH extracts. The structure elucidation of lipomelianol (**1**) and the identification of melianone (**4**) are described in this paper.

Melianone was identified (see Experimental) by comparison of its spectral data with those reported for an authentic sample,[8)] which has recently been defined as a mixture (**4**) of two epimers with respect to $C_{21}$ (in solution).[8b)] The established structure (**4**) of melianone was further corroborated by the high-resolution $^1$H-nuclear magnetic resonance ($^1$H-NMR) (400 MHz) spectral data (see Experimental) as well as the high-resolution $^{13}$C-NMR data (Table I; 100 MHz).

Lipomelianol (**1**), colorless fine crystals, mp 54—55 °C, $[\alpha]_D$ −3° ($CHCl_3$), showed typical ester bands (1725 and 1170 cm$^{-1}$) in its infrared (IR) spectrum and gave four molecular ion peaks at *m/z* 738 ($R^1$=–H, –*O*-stearoyl in formula **1**), 710 ($R^1$=–H, –*O*-palmitoyl), 682 ($R^1$=–H, –*O*-myristoyl), and 654 ($R^1$=–H, –*O*-lauroyl) in its field desorption mass spectrum (FD-MS). The electron impact mass spectrum (EI-MS) and accurate MS of **1** showed the fragment ion of highest mass number at 439.323 [$C_{29}H_{43}O_3$=439.321 (M−fatty acid unit−$CH_3$)$^+$],[9)] ascribable to the triterpene part of **1**. These spectral data suggested that **1** is an ester mixture consisting of a triterpene alcohol and four different types of higher fatty acid residues.



**1**: $R^1$ = α-H, β-$OCO(CH_2)_nCH_3$; $n$ = 10, 12, 14, 16
$R^2$ = H, OH; $C_{21}$ epimeric mixture
**2**: $R^1$ = α-H, β-$OCO(CH_2)_nCH_3$; $n$ = 10, 12, 14, 16
$R^2$ = O
**3**: $R^1$ = α-H, β-OH, $R^2$ = H, OH; $C_{21}$ epimeric mixture
**3a**: $R^1$ = α-H, β-OH, $R^2$ = α-OH, β-H
**4**: $R^1$ = O, $R^2$ = H, OH; $C_{21}$ epimeric mixture
**5**: $R^1$ = α-H, β-OAc, $R^2$ = H, OH; $C_{21}$ epimeric mixture

Chart 1

TABLE I. Carbon-13 Chemical Shifts (100 MHz, in $CDCl_3$, δ c)[a]

| Carbon | 1 | 3 | 4 |
|---|---|---|---|
| C-1 | 36.81 | 37.28 | 38.52 |
| C-2 | 23.82 | 27.70 | 35.12[b] |
| C-3 | 80.77; 80.74 | 79.24 | 216.79; 216.73 |
| C-4 | 37.92 | 39.03 | 47.88 |
| C-5 | 50.91[c]; 50.85[c] | 50.85[c]; 50.82[c] | 52.46; 52.40 |
| C-6 | 23.21 | 23.27 | 23.25 |
| C-7 | 118.06; 117.97 | 118.28; 118.17 | 118.18; 118.09 |
| C-8 | 145.72; 145.54 | 145.71; 145.53 | 145.78; 145.63 |
| C-9 | 49.67; 48.69 | 49.67; 48.88 | 49.64; 48.42 |
| C-10 | 34.96 | 35.11 | 34.91 |
| C-11 | 17.58 | 17.64 | 17.76 |
| C-12 | 35.20 | 35.23 | 35.19[b] |
| C-13 | 43.82; 43.63 | 43.87; 43.69 | 43.81; 43.59 |
| C-14 | 50.79[c]; 50.54[c] | 50.79[c]; 50.52[c] | 50.82; 50.46 |
| C-15 | 34.26 | 34.32 | 34.31 |
| C-16 | 27.46; 27.13 | 27.40; 27.17 | 27.47; 27.32 |
| C-17 | 47.13; 45.25 | 47.17; 45.24 | 47.09; 45.23 |
| C-18 | 13.12 | 13.15 | 12.75 |
| C-19 | 24.24 | 24.06 | 24.56 |
| C-20 | 33.83; 31.94 | 33.90; 31.90 | 33.80; 31.69 |
| C-21 | 101.85; 97.84 | 101.83; 97.80 | 101.82; 97.78 |
| C-22 | 31.54; 31.46 | 31.61; 31.49 | 31.54; 31.33 |
| C-23 | 78.49; 77.08 | 78.50; 77.02 | 78.45; 77.05 |
| C-24 | 67.77; 65.39 | 67.85; 65.49 | 67.76; 65.39 |
| C-25 | 57.99; 57.24 | 57.97; 57.24 | 57.98; 57.23 |
| C-26[d] | 25.03; 24.94 | 25.05; 24.99 | 25.02; 24.92 |
| C-27[d] | 19.46; 19.23 | 19.51; 19.30 | 19.46; 19.22 |
| C-28 | 27.61 | 27.55 | 24.41 |
| C-29 | 15.94 | 14.80 | 21.59 |
| C-30 | 22.69 | 22.64 | 22.62 |
| OCOR | 173.69 | | |

*a*) The 22.63 MHz data of compound **4** and related tirucallane-type triterpenoids were described in ref. 8*b* and the present assignments were based in part on these data. *b, c*) Values within any column may be interchanged. *d*) Assignments for C-26 and C-27 may be reversed in each column.

Alkaline hydrolysis of **1** gave a known $\Delta^7$-tirucallane-type triterpene alcohol, melianol (**3**), and a mixture of fatty acids, the acid composition of which was clarified as follows. The EI-MS and accurate MS of the mixture were indicative of the presence of stearic, palmitic, myristic, and lauric acids in the acid mixture. In addition, the corresponding methyl ester mixture was analyzed by gas-liquid chromatography-mass spectrometry (GC-MS), and its components were decided to be methyl stearate, palmitate, myristate, and laurate in a ratio of *ca.* 3 : 35 : 32 : 30.

The other hydrolysate, melianol, colorless needles, mp 207—208 °C, was shown to be identical with an authentic natural sample[8a] by direct comparison of their mps (mixed mp 208—210 °C; authentic sample, mp 209—211 °C), IR (KBr), EI-MS, and $^1$H-NMR (400 MHz) spectra, and thin layer chromatographic (TLC) behavior. The optical rotation value ($[\alpha]_D$ −33 °) was also consistent with that reported for an authentic specimen.[8a] For melianol, Lavie *et al.* have proposed the $C_{21}$ α-OH structure (**3a**).[8a] However, our $^1$H-(400 MHz; see Experimental) and $^{13}$C-NMR (100 MHz; Table I) spectral data demonstrated that melianol is a $C_{21}$ epimeric mixture as shown in formula **3** [or melianol exists in solution as the mixture (**3**)], like melianone (**4**),[8b] turraeanthin (**5**),[10] and other known tirucallane-type triterpenes having a similar hemiacetal side chain.[11]

In the $^1$H-NMR (400 MHz) spectrum of lipomelianol (**1**), each of 21-H, 23-H, and 24-H on the melianol part was observed as a pair (*ca.* 1 : 1) of signals (total, one proton) at δ 5.33 (d) and 5.37 (d), δ 3.85 (m) and 3.95 (m), and δ 2.71 (d) and 2.86 (d), respectively; this is due to the two possible hemiacetal structures (at $C_{21}$) of the melianol part of **1**. These $C_{21}$ epimeric structures of the melianol part of **1** were further corroborated by the $^{13}$C-NMR data (Table I) of **1** and by the following chemical transformation. Oxidation of **1** with chromium trioxide–pyridine gave the corresponding γ-lactone (**2**), which showed an intense γ-lactone carbonyl band (1785 cm$^{-1}$) as well as an ester carbonyl band (1730 cm$^{-1}$) in the IR spectrum. In the $^1$H-NMR spectrum of **2**, the hemiacetal proton signals (21-H) observed in **1** were absent, and on the other hand, a triple doublet at δ 4.16 (1H, $J$ = 10.5, 7.5, and 6.1 Hz, 23-H), a doublet at δ 2.82 (1H, $J$ = 7.5 Hz, 24-H), and seven well-resolved methyl singlets, ascribable to the triterpene framework of **2**, were observed.

The 3α-H signal (δ 4.52) of the ester (**1**) exhibited a downfield shift by *ca.* 1.3 ppm compared with that (δ 3.24) of the corresponding alcohol (**3**). This $^1$H-NMR result, coupled with the chemical transformation of **1** into **2**, indicates that in **1**, the fatty acids are connected with the 3β-OH group of **3** through an ester bond.

Based on the accumulated evidence, lipomelianol is now defined as a mixture (*ca.* 3 : 35 : 32 : 30) of the 3-*O*-stearate, palmitate, myristate, and laurate of melianol (**3**), as represented by formula **1**.

## Experimental

All melting points were determined on a Yanagimoto micro-apparatus and are uncorrected. IR spectra were run with a JASCO A-302 or a JASCO A-102 instrument. $^1$H-NMR spectra were measured with a JEOL GX-400 (400 MHz) spectrometer and $^{13}$C-NMR spectra with JEOL GX-400 (100 MHz) and/or JNM-FX 90Q (22.63 MHz) spectrometers with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. EI-MS and accurate MS were taken with a JEOL JMS DX-300 mass spectrometer equipped with a direct inlet system at 70 eV, and FD-MS spectra with the same mass spectrometer using carbon emitters under the following conditions: accelerating voltage, 3 kV; emitter current, 15—29 mA; and chamber temperature, room temperature. Optical rotations were determined for solutions in $CHCl_3$ on a JASCO DIP-140 digital polarimeter. GC-MS was carried out on a Hitachi RMU-6MG gas chromatograph equipped with a total ion monitor (detector) and a Hitachi M-80 mass spectrometer under the following operating conditions: column, 3% OV-275 on Chromosorb WAW DMCS (60—80 mesh; 2 m × 3 mm i.d.); column temperature, programmed from 152 to 242 °C at 10 °C/min; interface temperature, 240 °C; He flow rate, 5 ml/min; ionization energy, 30 eV; ion accelerating voltage, 3 kV; ionizing chamber temperature, 200 °C. For column chromatography and TLC, Merck Kieselgel 60 (230—400 mesh) and pre-coated silica gel plates (Merck HF-254) were used, respectively.

**Plant Material**——Fruits of *Melia toosendan* were collected in 1983 at the Medicinal Plant Garden of Osaka University (Faculty of Pharmaceutical Sciences, Suita, Osaka, Japan) and identified by Dr. K. Yoneda, Faculty of Pharmaceutical Sciences, Osaka University.

**Isolation of 1 and 4**——The dried fruits (2 kg) were crushed and extracted twice with MeOH (6 l) at room temperature for 10 d, and the solvent was evaporated off under reduced pressure. The combined extracts (262.5 g) were suspended in $H_2O$ and the aqueous suspension was extracted successively with petroleum ether (500 ml × 3; for defatting) and $CHCl_3$ (500 ml × 3). The $CHCl_3$ layer was dried over $MgSO_4$ and evaporated to give a residue (21.7 g),

a portion (21.0 g) of which was chromatographed on silica gel (800 g), eluting successively with $CHCl_3$ and $CHCl_3$–MeOH (99 : 1). The less polar fraction (970 mg) obtained by elution with $CHCl_3$ was separated again by silica gel column chromatography (30 g), and elution with hexane–AcOEt (2 : 1) afforded lipomelianol (**1**) (100 mg), colorless fine crystals, mp 54—55 °C (MeOH–$CHCl_3$), $[\alpha]_D^{20}$ −3.0° ($c$=0.18). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3300 (OH), 2920, 2850, 1725 (ester carbonyl), 1460, 1380, 1170, 1010, 970. $^1$H-NMR $\delta$: 5.37 (t)[12] and 5.33 (t)[12] (total 1H, H-21), 5.26 (1H, m, H-7), 4.52 (1H, dd, $J$=10.8, 4.2 Hz, H-3α), 3.95 (m) and 3.85 (m) (total 1H, H-23), 2.86 (d, $J$=7.7 Hz) and 2.71 (d, $J$=7.7 Hz) (total 1H, H-24), 1.34, 1.32, 1.31, 1.00, 0.99, 0.94, 0.85, 0.84, 0.77 (total 21H, all s, 7 × *tert*-Me), 0.88 [total 3H, t, $J$=6.8 Hz, Me$(CH_2)_n$COO-($n$=10, 12, 14, and 16)]. $^{13}$C-NMR: given in Table I. FD-MS $m/z$ (%): 738 ($M^+$, 17), 710 ($M^+$, 100), 682 ($M^+$, 66), 654 ($M^+$, 41). EI-MS $m/z$ (%): 710 ($M^+$, 3), 682 ($M^+$, 2), 654 ($M^+$, 2), 439 (28), 421 (33), 367 (99), 349 (25), 281 (30), 166 (100). Accurate MS: Found 439.323. Calcd for $C_{29}H_{43}O_3$, (M − fatty acid unit − $CH_3$)$^+$ (see formula **1**): 439.321. The polar fraction (800 mg) obtained from the first silica gel column with $CHCl_3$–MeOH (99 : 1) afforded, after recrystallization, melianone (**4**) (290 mg), colorless needles, mp 214—215 °C (MeOH) and 213 °C ($CHCl_3$–pentane) [ref. 8*b*, mp 212—214 °C ($CHCl_3$–pentane)], $[\alpha]_D^{20}$ −50.9° ($c$=0.11) [ref. 8*b*, $[\alpha]_D$ −48° ($CHCl_3$)]. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3450, 1700 (C=O), 1380, 1370, 810. $^1$H-NMR $\delta$: 5.38 (t)[13] and 5.30[14] (m) (total 1H, H-21), 5.30[14] (1H, m, H-7), 3.95 (m) and 3.85 (m) (total 1H, H-23), 2.86 (d, $J$=7.7 Hz) and 2.71 (d, $J$=7.7 Hz) (total 1H, H-24), 1.34, 1.31, 1.30, 1.12, 1.05, 1.03, 1.01, 0.90, 0.85 (total 21H, all s, 7 × *tert*-Me). $^{13}$C-NMR (100 MHz): given in Table I. MS $m/z$ (%): 470 ($M^+$, 41), 437 (72), 399 (12), 383 (100), 365 (64), 297 (45), 271 (30), 166 (27), 95 (32). Melianone was identified by comparison of its mp, optical rotation, IR, $^{13}$C-NMR (22.63 MHz), and EI-MS spectral data with those[8b] reported for an authentic specimen (**4**).

**Oxidation of 1**——$CrO_3$–pyridine complex [freshly prepared from $CrO_3$ (400 mg) and pyridine (20 ml)] was added to a solution of **1** (100 mg) in pyridine, and the mixture was stirred at room temperature for 4 d, then poured into ice-water, and extracted with $Et_2O$. The $Et_2O$ layer was washed with $H_2O$, dried over $MgSO_4$, and concentrated. The residue (91 mg) was subjected to silica gel column chromatography. Elution with hexane–AcOEt (3 : 1) gave the corresponding $C_{21}$ carbonyl derivative (**2**), a white powder, $[\alpha]_D^{20}$ −8.6° ($c$=0.18). IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 1785 (γ-lactone), 1730 (ester carbonyl), 1470, 1380, 1170, 1010. $^1$H-NMR $\delta$: 5.27 (1H, m, H-7), 4.52 (1H, dd, $J$=11.2, 4.2 Hz, H-3α), 4.16 (1H, ddd, $J$=10.5, 7.5, 6.1 Hz, H-23), 2.82 (1H, d, $J$=7.5 Hz, H-24), 1.38 and 1.35 (3H each, both s, Me-26 and -27), 1.04, 0.94, 0.85, 0.83, 0.78 (3H each, all s, 5 × *tert*-Me), 0.88 [total 3H, t, $J$=6.8 Hz, Me$(CH_2)_n$COO- ($n$=10, 12, 14, and 16)]. Elution of the silica gel column with hexane–AcOEt (2 : 1) afforded the starting material (**1**) (19 mg).

**Alkaline Hydrolysis of 1**——The ester (**1**) (80 mg) in 2% NaOMe–MeOH (20 ml) was stirred at room temperature for one day. The reaction mixture was poured into ice-water, neutralized with 5% aqueous HCl, and extracted with $Et_2O$. The $Et_2O$ solution was washed with $H_2O$, dried over $MgSO_4$, and concentrated. The residual product mixture was fractionated on a silica gel column with hexane–AcOEt (2 : 1) and (1 : 1) as eluting agents. The hexane–AcOEt (2 : 1) eluate gave, after evaporation of the solvents, a mixture of four higher fatty acids (14.5 mg), EI-MS and accurate MS $m/z$ (%): 284.272 ($M^+$ for stearic acid, 11) (Calcd for $C_{17}H_{35}COOH$: 284.272), 256.241 ($M^+$ for palmitic acid, 100) (Calcd for $C_{15}H_{31}COOH$: 256.240), 228.209 ($M^+$ for myristic acid, 40) (Calcd for $C_{13}H_{27}COOH$: 228.209), 200.179 ($M^+$ for lauric acid, 8) (Calcd for $C_{11}H_{23}COOH$: 200.178). This acids mixture was converted by $CH_2N_2$ treatment into a mixture of the corresponding methyl esters, the composition of which was decided by GC-MS to be methyl stearate, palmitate, myristate, and laurate in a ratio of *ca.* 3 : 35 : 32 : 30. The hexane–AcOEt (1 : 1) eluate from the silica gel column was further purified on a second silica gel column with $CHCl_3$–acetone (10 : 1) to give melianol (**3**) (44 mg), mp 207—208 °C (hexane–acetone) (authentic melianol,[8a] mp 209—211 °C), $[\alpha]_D^{20}$ −33° ($c$=0.07) (ref. 8*a*, $[\alpha]_D$ −38°). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: see ref. 8*a*; $\nu_{max}^{KBr}$ $cm^{-1}$: 3400 (OH), 1630 (w), 1440, 1380, 1035, 980, 810. $^1$H-NMR $\delta$: 5.37 (d, $J$=3.1 Hz) and 5.32 (d, $J$=2.3 Hz) (total 1H, H-21), 5.27 (1H, m, H-7), 3.95 (m) and 3.85 (m) (total 1H, H-23), 3.24 (1H, dd, $J$=11.2, 4.2 Hz, H-3α), 2.84 (d, $J$=7.5 Hz) and 2.70 (d, $J$=7.5 Hz) (total 1H, H-24), 1.33, 1.31, 1.30, 1.00, 0.99, 0.97, 0.90, 0.86, 0.85, 0.75 (total 21H, all s, 7 × *tert*-Me). $^{13}$C-NMR: see Table I. EI-MS and accurate MS $m/z$ (%): 472.355 [$M^+$, Calcd for $C_{30}H_{48}O_4$ (M) 472.355, 50], 439.321 [(M − $H_2O$ − $CH_3$)$^+$, Calcd for $C_{29}H_{43}O_3$ (M − $H_2O$ − $CH_3$) 439.321, 90], 385 (86), 367 (100), 299 (31), 166 (70). The mp (mixed mp 208—210 °C), IR (KBr), EI-MS, and $^1$H-NMR (400 MHz) spectra, and *Rf* value on TLC were identical with those of authentic melianol[8a] on direct comparison.

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## References and Notes

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6) This new compound (**1**) was, after the structure elucidation, defined as an ester mixture consisting of four different long-chain fatty acids and a $\Delta^7$-tirucallane-type triterpene alcohol, melianol (**3**), and hence, it was termed lipomelianol, by analogy with a series of lipo-alkaloids: lipoaconitine, *etc.*[7] Although **1** is a mixture, as described above, it behaved as a single compound in recrystallization and also in chromatography (column chromatography and TLC).
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9) The fragment ion of highest mass number (90%), observed in the EI-MS and accurate MS of melianol (**3**), had the same elemental composition, $C_{29}H_{43}O_3$ (Calcd: 439.321) (see Experimental).
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12) Both of these signals (t) collapsed to doublets [$\delta$ 5.37 ($J$=3.1 Hz) and 5.33 ($J$=3.3 Hz)] on deuteriation.
13) Signal (t) collapsed to a doublet ($J$=3.1 Hz) on deuteriation.
14) These signals were overlapping, and were observed as a multiplet.