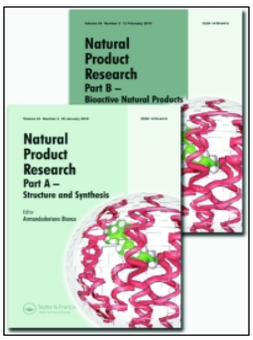

Natural Product Research

Formerly Natural Product Letters

ISSN: 1478-6419 (Print) 1478-6427 (Online) Journal homepage: http://www.tandfonline.com/loi/gnpl20

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To cite this article: Mangala Gowri Ponnapalli, Nalini Dangeti, Madhu Babu Sura, Haribabu Kothapalli, V. S. Sarma Akella & Jeelani Basha Shaik (2017) Self gelating isoracemosol A, new racemosaceramide A, and racemosol E from Barringtonia racemosa, Natural Product Research, 31:1, 63-69, DOI: 10.1080/14786419.2016.1212033

To link to this article: http://dx.doi.org/10.1080/14786419.2016.1212033

NATURAL PRODUCT RESEARCH, 2017
VOL. 31, NO. 1, 63–69
http://dx.doi.org/10.1080/14786419.2016.1212033

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Self gelating isoracemosol A, new racemosaceramide A, and racemosol E from *Barringtonia racemosa*

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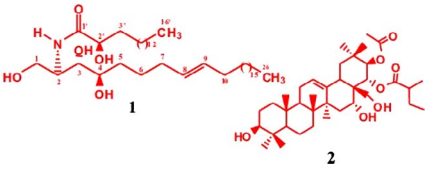
ABSTRACT

Phytochemical investigation of the $CHCl_3$ extract of the fruits of *Barringtonia racemosa* resulted in the isolation of two new metabolites along with isoracemosol A and betulinic acid as known metabolites. The new compounds were characterized as phytosphingosine-type ceramide [(2*S*,3*S*,4*R*)-2-[(2*R*)-2-hydroxyhexadecanoyl amino]-hexacos-8(*E*)-ene-1,3,4-triol, **1**] and racemosol E [21β-acetoxy-22α-(2-methylbutyroxy)-olean-12-ene-3β,16α,28-triol, **2**] on the basis of extensive spectroscopic data analysis and chemical modifications. In addition, the self gelating property of isoracemosol A (3) was investigated for the first time, which leads to the unexpected agglomerated porous like morphology.



ARTICLE HISTORY
Received 9 February 2016
Accepted 6 June 2016

KEYWORDS
Barringtonia racemosa; racemosaceramide A; racemosol E; isoracemosol A; morphology and gelating property

1. Introduction

Recently, pentacylic triterpenoids of lupane (Braga Gopal & Shib Shankar 2011) and oleanane (Braga Gopal et al. 2006) triterpenoids (O'Neill et al. 2005) have been emerged as supramolecular architectures. Nature continues to offer enormous synthetic challenges, of which acylated polyhydroxy triterpenoids are rather unusual and difficult to manipulate synthetically. Plants belonging to the *Barringtonia*, (Clive et al. 2005; Consolacion et al. 2012) and *Foetidia* (Marie-Laure et al. 2002) genera of Lecythidaceae family were found to be a rich source of acylated triterpenoids. As part of our ongoing program on isolation of bioactive metabolites from Indian mangrove flora (Gowri et al. 2009; Ponnapalli et al. 2012; Annam

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Supplemental data for this article can be accessed here at http://dx.doi.org/10.1080/14786419.2016.1212033.

et al. 2015; Sura et al. 2015), we have investigated metabolites from *Barringtonia racemosa*. It grows on the west coast of India and has been used as a folk medicine for several ailments ranging from stomach complaints to fever, rheumatoidal arthritis (Jayaweera 1981) and cancer (Deraniyagala et al. 2003). Herein, we report the isolation and structure elucidation of a ceramide termed as racemosaceramide A (**1**) and racemosol E (**2**) along with two known compounds isoracemosol A (**3**) and betulinic acid (4) (Yang et al. 2006). In addition, the gelating behaviour of isoracemosol A was investigated for the first time, which leads to the unexpected agglomerated porous like morphology that brings accessibility for designing new functional materials.

2. Results and discussion

Racemosaceramide A (**1**) was obtained as an amorphous powder with optical rotation, $[\alpha]_D^{27}$ +20.2 (*c* 0.3, Py). Its molecular formula was determined as $C_{42}H_{83}NO_5$ on the basis of pseudomolecular ion peak at *m/z* 704.6174 $[M + Na]^+$ in HR-ESIMS and FAB MS. Its IR spectrum demonstrated absorption bands for hydroxy, olefinic and amide groups.

The 1D NMR data (Table S1) of **1** indicated the presence of an amide proton doublet at δ_H [8.57 (1H, d, J = 8.8 Hz); δ_C 174.9], two olefinic proton signals at δ 5.50 (2H, m), and protons of two different long methylene chains at δ 1.28 with terminal methyl groups at [δ_H 0.88 (6H, t, J = 7.9 Hz) δ_C 14.0] indicating a phytosphingosine-type ceramide (Takahiro et al. 2006). The characteristic resonances of 2-amino-1,3,4-triol of the sphingosine unit were observed at [δ_H 4.49 (1H, dd J = 4.9, 3.8 Hz); δ_C 61.7], δ_H [4.40 (1H, dd, J = 4.9, 10.8 Hz); δ_C 76.5], δ_H [4.32 (1H, m); δ_C 72.6], δ_H 4.27 (1H, m); δ_C 72.2].

Methanolysis of **1** afforded a fatty acid methyl ester (FAME), and a long-chain base. The FAME was identified as methyl-2-hydroxyhexadeconoate ($[M^+]$ 286) by means of GCMS analysis and the absolute configuration at C-2 was determined to be *R* from the specific rotation (Shibuya et al. 1990) and also the negative Cotton effect at 215 nm in its CD spectrum (Craig & Lee 1977). The presence of a hydroxy group in the α-position was ascertained by comparison of spectral data with reported data (Shibuya et al. 1990). The presence of a 1,3,4-trihydroxy unsaturated long-chain base was deduced from the ^1H–^1H COSY spectrum. The position of the double bond in the long chain base was established by the characteristic fragment ions at *m/z* 403, 459 in FAB-MS due to allylic cleavage (Figure S3) and also by EIMS analysis of the corresponding dimethyl sulphide derivative of compound **1** (Stothers 1972). The characteristic fragment ion at *m/z* 299, indicated the double bond was located at C-8. The chemical shifts of the allylic methylene carbons in **1** were assigned at δ_C 33.5 (C-7 or C-10) and 33.1 (C-7 or C-10) based on the clearly observed HMBC correlations from olefinic protons to C-7 and C-10. The geometry of the double bond was ascertained to be *trans* according to the chemical shifts of the allylic carbons (Stothers 1972). The sequence of C-1 to C-5 moiety in **1**, which includes **3** hydroxyls and an amide group (Figure 1) was established by a DQF-COSY experiment (Table S2 and Figure S2) which correlated all the corresponding protons, including the NH signal. Analysis of the ^1H–^1H COSY, HSQC, and HMBC spectra (Table S2 and Figure S1) led to the assignment of all the corresponding proton and carbon signals for **1**. The correlations from δ_H 8.57 (NH) to δ_C 174.9 (C-1′, s), 72.2 (C-2′, d), 61.7 (C-1, t). 52.7 (C-2, d), and 76.5 (C-3, d) were observed in the HMBC spectrum of **1**. These correlations established the location of the amide group in compound **1**

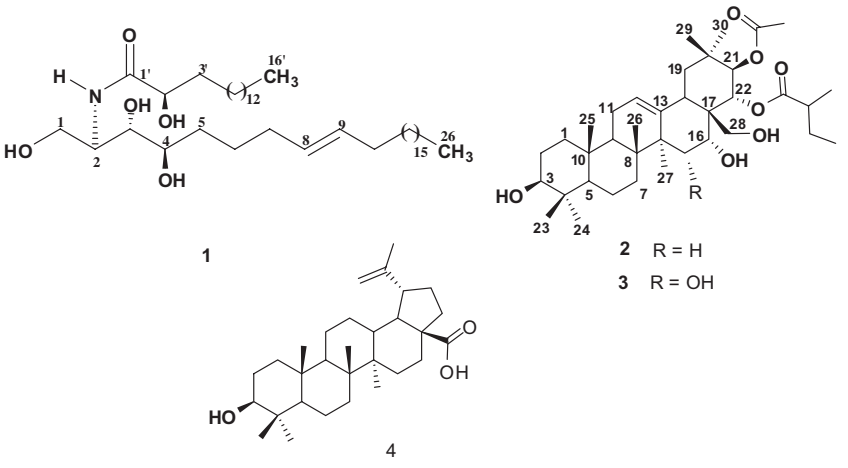

Figure 1. Compounds isolated from the fruits of *Barringtonia racemosa*.

The chemical shifts of H-2 (δ 5.10, 1H, m), H-3 (δ 4.32, 1H, m), and H-4 (δ 4.27, 1H, m) in C_5D_5N were in good agreement with those of known synthetic ceramide (2*S*,3*S*,4*R*)-2-[(2*R*)-2-hydroxytetracosanoylamino]-hexadecane-1,3,4-triol and natural ceramide gracilamide B (Yi et al. 2006). The absolute stereochemistry of the ceramide moiety was presumed to be 2*S*, 3*S*, 4*R*, 2*R* by comparison of specific rotation with asteriaceramide A (Takahiro et al. 2006). Thus, the structure of compound **1** was unequivocally established as (2*S*,3*S*,4*R*)-2-[(2*R*)-2-hydroxyhexadecanoyl amino]-hexacos-8(*E*)-ene-1,3,4-triol.

Racemosol E (2) was obtained as an amorphous solid, $[\alpha]_D^{27}$ +2.5 (*c* 0.006, Py). Its HR-ESIMS showed a pseudo molecular ion peak at *m/z* 639.4259 $[M + Na]^+$ (Calcd 639.4231, which corresponded to a molecular formula $C_{37}H_{60}O_7$ with 8° of unsaturation. Its IR spectrum revealed absorption bands for hydroxy, an ester carbonyl, and olefinic functionalities. The ^{1}H NMR spectrum (Table S1) revealed the presence of seven tertiary methyl groups, one trisubstituted olefinic proton at δ 5.44 (1H, t, *J* = 3.3 Hz). Furthermore, four oxymethines, an oxymethylene, an acetyl and 2-methylbutyryl groups were evident from its ^{1}H NMR spectrum. The ^{13}C NMR spectrum (Table S1) displayed 37 carbon resonances, which were analysed as 10 methyls, 9 methylenes, 9 methines and 9 quaternary carbon atoms from its DEPT and HSQC spectra. A preliminary analysis of the ^{1}H and ^{13}C NMR data (Table S1) revealed that two possess an acylated olean-12-ene structural framework. The ^{1}H–^{1}H COSY (Table S2 and Figure S1) correlations from H-1 to H-2 and H-5 to H-6 were suggestive to determine the sequence of C1-C5 moiety in **2**. Moreover, the presence of 2-methyl butanoyl moiety was confirmed based on observed 2′-H to 3′-H, 4′-H, 5′-H COSY correlations. The HMBC (Table S2 and Figure S1) correlations from H-21 to the acetyl carbonyl carbon and from H-22 to C-1′ confirmed the location of an acetyl and a 2-methyl butanoyl groups in the pentacarbocyclic architecture of olean-12-ene. Upon alkaline hydrolysis, compound **2** formed barringtogenol C, which was identified by spectroscopic data as well as by comparison with authentic sample and reported data (Crublet et al. 2002). Compound **2** was characterized as an acyl derivative of baringtogenol C. The location of the hydroxyls at C-3, C-16, C-28 was further confirmed by HMBC correlations of H-3/C-23, C-24; H-16/C-14, C-18; and H2-28/C-17, C-18, C-22 respectively.

The relative configuration of two was determined by NOESY correlations (Table S2, Figure S2) and also by coupling constant. The NOESY spectrum of **1** showed cross-peaks of H-3/H_3-23; H-21/H_3-30; H-22/H_3-29, H-16/H_3-26, 28-Ha. These were used to postulate the relative configuration of stereogenic centres in **2**. Consequently, the structure of compound **2** was determined as 21β-acetoxy-22α-(2-methylbutyroxy)-olean-12-ene-3β,16α,28-triol (**2**).

2.1. Gelation behaviour

We have studied the gelation property of isoracemosol A in a wide range of aliphatic (acyclic and cyclic) and aromatic organic solvents (See Supporting Information). The gelating behaviour of compound **3** is summarised in Table (See Supporting Information). Isoracemosol A, a naturally occurring diacylated polyhydroxy triterpenoid possesses weak amphiphilic character to induce self assembly in CCl_4. However, at higher concentrations it was possible to get strong gel upon slight warming (at 60 °C) in CCl_4 after keeping the solution at room temperature for 30 min. Moreover, we have extended the gelation efficiency of compound **3** in mixture of *n*-hexane and acetone (See Supporting Information) and the results are depicted in Table (See Supporting Information).

2.2. Thermal stability of the gel

The thermal stability of the organogel of **3** was checked in a mixture of solvents by the 'inverted test tube method' (Babu & Maitra 2005). Compound (**3**) showed thermal stability (0.2 w/v%) in mixture of *n*-hexane and acetone 88:12. The T_{gel} vs. concentration plots (See Supporting Information) indicated that for the same concentration range, the thermal stabilities were, 88:12 > 86:14 > 90:10 proportions of *n*-hexane and acetone.

2.3. Morphology

The morphology of bare compound and gel derived from isoracemosol A was investigated by Scanning Electron Microscopy (SEM) (Figure S3). The SEM micrograph did not reveal any regular fibrous structures. Bare compound **3** only showed stone-like morphology, while its gel exhibited agglomerated porous-like structure, which is rather unusual. It can be suggested that hydrogen bonding interactions may be responsible for the agglomerated porous formation, as the molecules contain hydroxy groups.

3. Experimental

3.1. General experimental procedures

Optical rotations were measured on a Horiba SEPA-300 high sensitive Polarimeter. IR spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer with K Br pellets. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded with a Bruker Avance II spectrometer in C_5D_5N with TMS as an internal standard. Coupling constants (*J*) were given in Hz. The ESIMS data were recorded on an Agilent 1100 MSD with an ESI SL trap. The HR-ESIMS data were acquired on an Agilent 6510 Q-TOF and ESI probe. Column chromatography was performed with silica gel (100–200, 230–400 mesh, Sigma). Silica gel F254 (0.25 mm, Merck) was

used for analytical TLC. Field Emission Scanning electron microscopy experiments were carried out using Zeiss Ultra Plus scanning electron microscope.

3.2. Plant material

Fruits of *B. racemosa* Roxb. were purchased from a local market in Trivandrum in March 2011 from Kerala, India, and authenticated by Prof B. Kondala Rao, Department of Marine Living Sources, Andhra University, Visakhapatnam. A voucher specimen (#IIC-MG-116) has been deposited in the Herbarium of Natural Products Chemistry, IICT, Hyderabad, India.

3.3. Isolation and identification

The fruits of (2.0 kg) *B. racemosa* were ground to a fine powder and extracted with $CHCl_3$ (10 L) in a Soxhlet apparatus for 18 h. After filtration, the filtrate was concentrated under reduced pressure to yield a pale yellow residue (26.7 g). A part of this residue (25 g) was subjected to silica gel (230–400 mesh, Merck) VLC and eluted with *n*-hexane:acetone mixtures of increasing polarity, resulted in 12 main fractions of 800 mL each. Fraction-6 was subjected to Si gel CC afforded racemosaceramide A (**1**, 10 mg). Fraction-8 was submitted to silica gel CC eluted with *n*-hexane–acetone (8:2) resulted in the isolation of racemosol E (**2**, 9 mg), isoracemosol A (**3**, 300 mg). Fraction 12 was repeatedly purified by silica gel CC using *n*-hexane–acetone (6:4) to obtain pure betulinic acid, **4** (20 mg).

3.3.1. Racemosaceramide A (1)

$C_{42}H_{83}NO_5$; white amorphous powder; $[\alpha]_D^{27}$ +20.2 (*c* 0.3, pyridine); IR (KBr) ν_{max} 3390 and 1070 cm^{-1} (hydroxy); 1633 cm^{-1} (amide); and 2917, 2849, 1470 cm^{-1} (aliphatic) functionalities; HR-ESIMS *m/z* $[M + Na]^+$ 704.6174 (Calcd mass for $C_{42}H_{83}NO_5$ 681.62712), and FAB MS *m/z* 705 $[M^+ + Na + H]$; ^1H NMR (600 MHz, C_5D_5N), δ: 8.57 (1H, d, J = 8.8 Hz, N–H), 1.28 (aliphatic C chain), 4.49 (1H, dd, J = 4.9, 3.8 Hz, H-1α), 4.40 (1H, dd, J = 4.9, 10.8 Hz, H-1), 5.10 (1H, m, H-2), 4.32 (1H, m, H-3), 4.27 (1H, m, H-4), 5.50 (2H, m, H-8/9), 4.61 (1H, dd, J = 3.6, 7.5 Hz, H-2′), 1.98 (5H, m, H-5β, H-4′α, H-8β, H-9β, H-3′β), 0.88 (6H, J = 7.9, H-18, H-24′); ^{13}C (150 MHz, C_5D_5N), δ: 174.9 (C-1′), 72.2 (C-2′), 35.4 (C-3′), 25.6 (C-4′), 61.7 (C-1), 52.7 (C-2), 76.5 (C-3), 72.6 (C-4), 33.6 (C-5), 26.5 (C-6), 33.1 (C-7), 130.6 (C-8), 130.4 (C-9), 32.7 (C-10) and 2D NMR data (Table S2 and Figures S1–S2).

3.3.2. Racemosol E (2)

$C_{37}H_{60}O_7$; white amorphous solid; $[\alpha]_D^{27}$ +2.5 (*c* 0.06, pyridine); IR (KBr) ν_{max} 3452, 2942, 2853, 1732, 1648, 1463, 1377, 1245, 1086 cm^{-1}; HR-ESIMS *m/z* $[M + Na]^+$ 639.4259 (Calcd mass for $C_{37}H_{60}O_7$, 639.4231); ^1H NMR (600 MHz, C_5D_5N), δ: 1.58 (1H, m, H-1α), 1.03 (1H, m, H-1β), 1.87 (1H, m, H-2α), 3.47 (1H, dd, J = 5.1, 11.0 Hz, H-3), 0.88 (1H, d, J = 7.0 Hz, H-5), 1.57 (1H, m, H-6α), 1.39 (1H, m, H-6β), 1.62 (1H, m, H-7α), 1.33 (1H, m, H-7β), 1.78 (1H, m, H-9), 1.93 (1H, m, H-11α), 1.85 (1H, m, H-11β), 5.44 (1H, t, J = 3.3 Hz, H-12), 2.02 (1H, m, H-15α), 1.64 (1H, m, H-15β), 4.48 (1H, br s, H-16), 3.08 (1H, m, H-18), 3.08 (1H, m, H-19α), 1.41 (1H, m, H-19β), 6.54 (1H, d, J = 10.1, H-21), 6.28 (1H, d, J = 10.1, H-22), 1.25 (3H, s, H-23), 0.92 (3H, s, H-24), 0.91 (3H, s, H-25), 1.05 (3H, s, H-26), 1.81 (3H, s, H-27), 3.68 (1H, d, J = 10.5, H-28a), 3.42 (1H, d, J = 10.5, H-28b), 1.06 (3H, s, H-29), 1.28 (3H, s, H-30), 2.10 (3H, s, H-21-$COCH_3$), 2.27 (1H, sext, J = 7.0 Hz, H-2′), 1.72 (1H, m, H-3′b), 0.79 (3H, t, J = 7.4 Hz, H-4′) 1.12 (3H, d, J = 7.0 Hz, H-5′);

^{13}C (150 MHz, C_5D_5N), δ: 39.1 (C-1), 28.1 (C-2), 78.0 (C-3), 40.1 (C-4), 55.8 (C-5), 18.8 (C-6), 33.2 (C-7), 39.4 (C-8), 47.1 (C-9), 37.2 (C-10), 23.9 (C-11), 123.0 (C-12), 142.9 (C-13), 41.7 (C-14), 34.8 (C-15), 68.3 (C-16), 48.2 (C-17), 40.1 (C-18), 47.2 (C-19), 36.3 (C-20), 79.3 (C-21), 73.5 (C-22), 28.7 (C-23), 16.9 (C-24), 16.6 (C-25), 16.9 (C-26), 27.4 (C-27), 63.6 (C-28), 29.4 (C-29), 20.1 (C-30), 170.8 (C-21-CO-CH_3), 21.2 (C-21-CO-CH3), 176.7 (C-1′), 41.7 (C-2′), 26.9 (C-3′), 11.9 (C-4′), 15.8 (C-5′) and 2D NMR data (Tables S1–S2 and Figures S1–S2).

3.4. DMDS Derivative of (1)

Compound **1** (0.5 mg) was dissolved in CS_2 (0.2 mL) with the addition of dimethyl disulfide (DMDS) (0.2 mL) and 20 µL of iodine solution (60 mg of I_2 IN 1 mL of diethyl ether). After stirring for 48 h at 60 °C in a 10 mL tube sealed with a Teflon-lined cap, the reaction mixture was diluted with 0.2 mL of $Na_2S_2O_3$ solution (5% in distilled water). The organic phase was refluxed and the aqueous phase was extracted twice with 0.2 mL of *n*-hexane. The organic extracts were concentrated, and the DMDS derivative was analysed by EIMS, which showed molecular ion peak at *m/z* 775.

4. Conclusion

This is the first report of occurrence of ceramide from Lecythidaceae family. In addition, the self gelating property of isoracemosol A was investigated for the first time, which leads to the unexpected agglomerated porous like morphology.

Supplementary material

Supplementary material relating to this article is available online, alongside Figures S1–S2 and Tables S1–S2.

Acknowledgement

We thank Dr S. Chandrasekhar, director, I.I.C.T. for constant support and encouragement.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Department of Science and Technology, New Delhi, India [grant number SR/S1/OC-33/2011].

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