

## Oleanane-Type Isomeric Triterpenoids from *Barringtonia racemosa*

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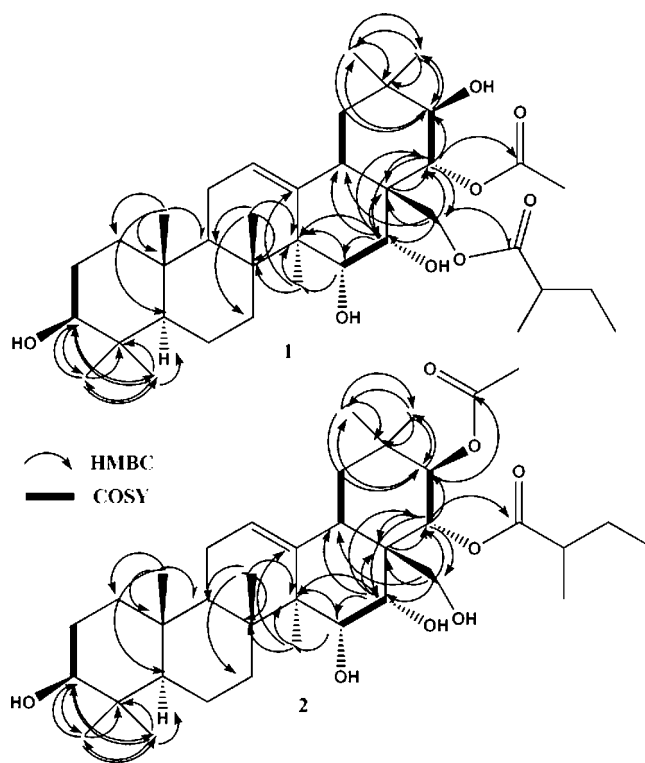
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Two new isomeric acylated oleanane-type triterpenoids along with three known compounds were isolated from the MeOH extract of the dried fruits of *Barringtonia racemosa*. On the basis of spectroscopic methods, with special emphasis on 1D and 2D NMR techniques as well as chemical methods, the structures were characterized as racemosol A (**1**) [22 $\alpha$ -acetoxy-3 $\beta$ ,15 $\alpha$ ,16 $\alpha$ ,21 $\beta$ -tetrahydroxy-28-(2-methylbutyryl)olean-12-ene] and isoracemosol A (**2**) [21 $\beta$ -acetoxy-3 $\beta$ ,15 $\alpha$ ,16 $\alpha$ ,28-tetrahydroxy-22 $\alpha$ -(2-methylbutyryl)olean-12-ene]. The isolated compounds (**1–5**) were not active against HeLa and P388 D1 carcinoma cell lines.

*Barringtonia racemosa* is an evergreen mangrove tree distributed in Bangladesh, Sri Lanka, and the west coast of India.<sup>1</sup> It has been used as a folk medicine to treat rat-snake bites, rat poisoning, boils, gastric ulcers, itch, piles, typhoid fever,<sup>2</sup> and cancer in certain remote villages of Kerala (India). Pharmacological studies on seed extracts of *B. racemosa* have shown anti-DLA and antitumor activities.<sup>3</sup> An extract of the leaves displayed cytotoxicity against HeLa carcinoma cell lines,<sup>4</sup> while extracts of the bark showed antinociceptive properties<sup>5</sup> and broad-spectrum antifungal activity,<sup>6</sup> and a diterpenoid, nasimalun A, displayed antibacterial activity.<sup>7</sup> Prior phytochemical studies on this plant have yielded 3,3'-dimethoxyellagic acid, dihydromyricetin, gallic acid, bartogenic acid, stigmaterol,<sup>8</sup> R<sub>1</sub>-barrigenol,<sup>9</sup> olean-18-en-3- $\beta$ -*O*-coumaroyl ester, and olean-18-en-3- $\beta$ -*O*-Z-coumaroyl ester, along with germanicol, germanicol, betulinic acid, lupeol, taraxerol,<sup>10</sup> and neo-clerodane-type diterpenoids nasimalun A and B.<sup>11</sup> In this paper, the isolation, structural elucidation, and the results of the cytotoxicity assay of two new isomeric triterpenes (**1**, **2**), including three known (**3–5**) compounds, are reported. In addition, three known compounds have been readily identified as stigmaterol (**3**),<sup>12</sup> barringtogenol C (**4**),<sup>13</sup> and bartogenic acid (**5**)<sup>14</sup> through analysis of their physical and spectroscopic data (IR, MS, <sup>1</sup>H NMR).

Racemosol A (**1**) was obtained as a white, amorphous powder. The HRESIMS of **1** exhibited the sodiated molecular ion peak at *m/z* 655.4157, to indicate a molecular formula of C<sub>37</sub>H<sub>60</sub>O<sub>8</sub> (calc 655.4180), which was confirmed by <sup>13</sup>C NMR and DEPT analysis. The IR spectrum of **1** showed absorption bands for olefinic (1648 cm<sup>-1</sup>), hydroxy (3426 cm<sup>-1</sup>), and ester (1738, 1709, 1243 cm<sup>-1</sup>) functionalities. The 1D spectra revealed the presence of signals for seven tertiary methyl groups resonating between  $\delta$  0.92 and 1.86 and one trisubstituted olefinic proton at  $\delta$  5.62 (1H, t, *J* = 3.4 Hz) with typical <sup>13</sup>C NMR resonances ( $\delta$  125.6 and 143.2) indicating an olean-12-ene triterpene derivative.<sup>15</sup> Its <sup>1</sup>H NMR spectrum exhibited one terminal methyl triplet [ $\delta$  0.92 (3H, t, *J* = 7.4 Hz, H-4')] and one secondary methyl doublet at  $\delta$  1.26 (3H, d, *J* = 6.9 Hz, H-5') attributed to a 2-methylbutanoyl (MB),<sup>16</sup> an acetyl at  $\delta$  1.87 (3H, s), and a characteristic downfield double doublet at  $\delta$  3.47 (*J*<sub>3ax, 2ax</sub> = 10.2 Hz, *J*<sub>3ax, 2eq</sub> = 5.4 Hz) attributable to an oxymethine proton. The <sup>13</sup>C NMR spectrum of **1** (C<sub>5</sub>D<sub>5</sub>N, 150 MHz) showed resonances for 37 carbon atoms, whose substitution patterns were revealed from DEPT and HSQC experiments as 10 methyls, eight methylenes, 10 methines, and nine quaternary carbons. It showed five oxymethine carbons at  $\delta$  67.4, 72.5, 76.1, 77.6, and 77.9



**Figure 1.** HMBC and COSY diagrams of compounds **1** and **2**.

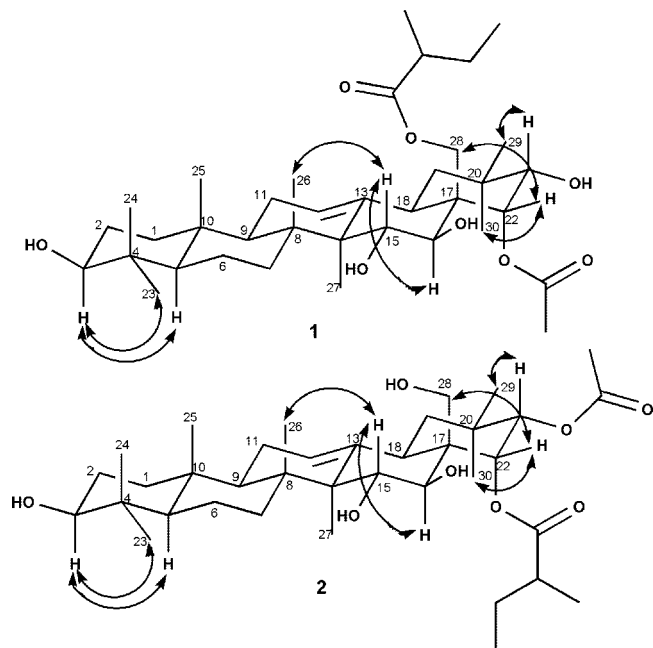
and one oxymethylene group at  $\delta$  67.0. The foregoing evidence suggested that one of the six oxygenated carbons was located at ring A and the remaining ones at rings D and E.<sup>17</sup> The presence of two pairs of doublets at  $\delta$  4.26 (d, *J* = 4.3 Hz, H $_{\beta}$ -15), 4.48 (br s, H $_{\beta}$ -16), 4.93 (d, *J* = 9.8 Hz, H $_{\alpha}$ -21), and 5.91 (d, *J* = 9.8 Hz, H $_{\beta}$ -22) in the <sup>1</sup>H NMR spectrum of **1** led to the placement of these four oxygenated carbons at C-15, C-16, C-21, and C-22.

Alkaline hydrolysis of **1** yielded R<sub>1</sub>-barrigenol (**1a**), the structure of which was elucidated on the basis of comparison of spectroscopic data with reported data.<sup>17</sup> The deshielding of H-22 ( $\delta$  5.91) and H-28 ( $\delta$  4.25, 4.08) of **1** compared with H-22 [ $\delta$  4.60 (d, *J* = 9.5 Hz)] and H-28 [ $\delta$  4.16 (d, *J* = 10.4 Hz), 3.79 (d, *J* = 10.4 Hz)] of **1a** indicated the positions of the acyl groups in **1**. In an HMBC experiment on **1**, the ester carbonyl signal at  $\delta$  170.9 gave a cross-peak with the methine proton (CH-22) at  $\delta$  5.91, confirming the acetyl group at C-22. Therefore, the 2-methylbutyryl group should be linked to C-28. This was also

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**Figure 2.** Key NOESY correlations of compounds **1** and **2**.

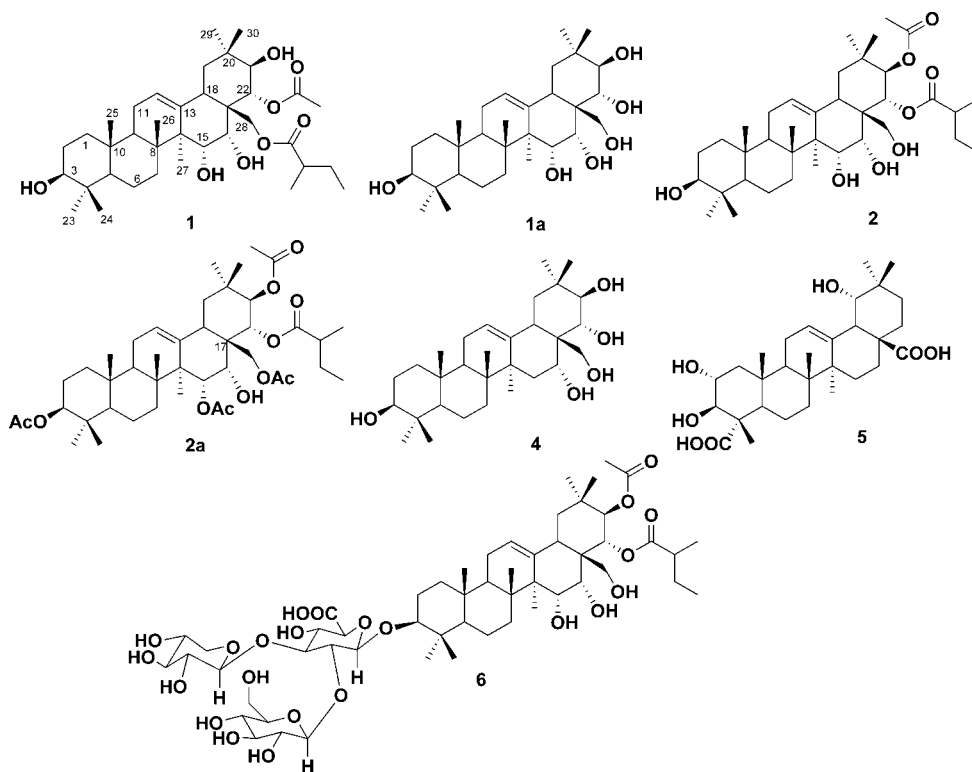
evident from the cross-peaks between the carbonyl carbon of 2-methylbutyryl and the C-28 methylene group in the HMBC spectrum (Figure 1, Table 3). Further analysis of HMBC data showed that correlations of Me-23 ( $\delta$  28.5) and Me-24 ( $\delta$  15.8) to C-3 ( $\delta$  77.9), C-4 ( $\delta$  39.2), and C-5 ( $\delta$  55.5) were used to position a hydroxy group at C-3. The C-18 methine proton [ $\delta$  2.86 (dd,  $J = 4.3, 14.3$  Hz)] showed HMBC couplings with C-17 ( $\delta$  46.2). The C-19 protons [ $\delta$  3.06 (t,  $J = 13.7$  Hz), 1.47 (m)] showed HMBC connectivities with C-20 ( $\delta$  36.6), C-18 ( $\delta$  42.0), C-29 ( $\delta$  30.0), and C-30 ( $\delta$  19.1).

In view of the close and comparable chemical shifts of the remaining carbons, in particular those of the stereogenic carbons

C-3, C-15, C-16, C-21, C-22, and C-28, with those of R<sub>1</sub>-barrigenol, the same relative configuration was assumed for racemosol A (**1**). This was further confirmed by its <sup>1</sup>H–<sup>1</sup>H NOESY spectrum (Figure 2, Table 3). The cross-peaks between H-21 ( $\delta$  4.93) and H-29 ( $\delta$  1.08) as well as between H-22 ( $\delta$  5.91) and H-30 ( $\delta$  1.41), and H-28 ( $\delta$  4.25, 4.08), suggested that H-21 and H-22 are  $\alpha$ - and  $\beta$ -axial, respectively. H-15 was correlated with the C-26 methyl protons ( $\delta$  1.21, s), indicating that the 15-OH group is  $\alpha$ -equatorial. The hydroxy groups at C-15 ( $\delta$  67.4) and C-16 ( $\delta$  72.5) were both assigned  $\alpha$ -orientations by comparison with literature <sup>13</sup>C NMR data.<sup>18,19</sup> In addition, the small coupling constant ( $J_{15,16} = 4.3$  Hz) suggested that H-15 and H-16 are both axially oriented. Thus, the structure of **1** was elucidated as 22 $\alpha$ -acetoxy-3 $\beta$ ,15 $\alpha$ ,16 $\alpha$ ,21 $\beta$ -tetrahydroxy-28-(2-methylbutyryl)olean-12-ene.

The molecular formula of **2** was determined to be C<sub>37</sub>H<sub>60</sub>O<sub>8</sub> by combination of the HRESIMS ion at  $m/z$  655.4224 (calc 655.4180) and <sup>13</sup>C NMR data. From its <sup>1</sup>H and <sup>13</sup>C NMR spectra, it was found to be isomeric to racemosol A (**1**) and thus designated as isoracemosol A. It exhibited strong hydroxy (3445 cm<sup>-1</sup>) and trisubstituted olefinic (1646 cm<sup>-1</sup>) IR absorptions similar to racemosol A (**1**). It gave a triacetate (**2a**), C<sub>43</sub>H<sub>66</sub>O<sub>8</sub>, on acetylation with pyridine and acetic anhydride, which still showed an IR hydroxy absorption at 3486 cm<sup>-1</sup>, in addition to acetate absorption (1739, 1238 cm<sup>-1</sup>) indicating the presence of three acylable hydroxy groups and a hindered secondary or tertiary hydroxy group. The H-16 resonance at  $\delta$  4.39 (1H,  $J = 4.3$  Hz) showed that this hindered position of isoracemosol A, similar to barringtogenol C,<sup>20</sup> was not acetylated. Its <sup>1</sup>H and <sup>13</sup>C NMR spectra closely resemble those of **1**. Seven tertiary methyls, acetyl, and 2-methylbutanoyl groups were evident from the <sup>1</sup>H NMR spectrum (see Table 1). Like racemosol A (**1**), it also exhibited 37 carbon signals, whose multiplicities were revealed by DEPT and HSQC spectra, and the chemical shift assignments were made by comparison with those of racemosol A (**1**). It showed five oxymethine carbons at  $\delta$  67.7, 73.1, 73.2, 78.0, and 79.4 and one oxymethylene group at  $\delta$  63.1, analogous to **1**. The presence of two pairs of doublets at  $\delta$  4.22 (d,  $J = 4.3$

**Chart 1**



**Table 1.**  $^1\text{H}$  NMR Data for Compounds **1**, **2**, and **2a**

proton no.	<b>1</b> <sup>a</sup>	<b>2</b> <sup>b</sup>	<b>2a</b> <sup>a</sup>
1 $\alpha$	2.12 (dt, 4.0, 13.6)	2.11 (m)	1.98 (m)
1 $\beta$	2.21 (td, 3.1, 13.8)	2.19 (m)	1.32 (m)
2 $\alpha$	1.86 (m)	1.85 (m)	
2 $\beta$			
3	3.47 (dd, 5.4, 10.2)	3.47 (dd, 5.3, 10.7)	4.71 (dd, 4.9, 11.7)
5	0.94 (m)	0.96(m)	0.90 (m)
6 $\alpha$	1.65 (m)	1.68 (m)	
6 $\beta$	1.47 (m)	1.49 (m)	
7 $\alpha$	1.64 (m)	1.64 (m)	
7 $\beta$	1.07 (m)	1.08 (m)	
9	1.80 (m)	1.79 (m)	
11 $\alpha$	1.99 (m)	1.97 (m)	1.89 (m)
11 $\beta$			1.63 (m)
12	5.62 (t, 3.4)	5.56 (t, 3.7)	5.59 (t, 4.1)
15	4.26 (d, 4.3)	4.22 (d, 4.3)	5.40 (d, 4.2)
16	4.48 (br s)	4.39 (d, 4.3)	4.75 (m)
18	2.86 (dd, 4.3, 14.3)	3.08 (m)	2.81 (dd, 5.1, 14.2)
19 $\alpha$	3.06 (t, 13.7)	3.08 (m)	3.10 (t, 13.9)
19 $\beta$	1.47 (m)	1.43 (m)	1.47 (m)
21	4.93(d, 9.8)	6.52 (d, 10.1)	6.42 (d, 10.1)
22	5.91(d, 9.8)	6.21 (d, 10.1)	5.87 (d, 10.1)
23	1.21 (s)	1.23 (s)	0.90 (s)
24	0.98 (s)	0.98 (s)	0.88 (s)
25	1.04 (s)	1.07 (s)	0.89 (s)
26	1.21 (s)	1.11 (s)	1.10 (s)
27	1.86 (s)	1.83 (s)	1.96 (s)
28a	4.25 (d, 11.5)	3.77 (d, 10.7)	4.32(d, 11.3)
28b	4.08 (d, 11.5)	3.49 (d, 10.7)	4.19(d, 11.3)
29	1.33 (s)	1.08 (s)	1.03(s)
30	1.41 (s)	1.29 (s)	1.22(s)
21-COCH <sub>3</sub>		2.12 (s)	2.18(s)
22-COCH <sub>3</sub>			
2'	2.49 (sext, 6.9)		
3'a	1.81 (m)	1.62 (m)	1.62 (m)
3'b	1.52 (m)	1.26 (m)	1.28 (m)
4'	0.92 (t, 7.4)	0.72 (t, 8.0)	0.79 (t, 7.4)
5'	1.26 (d, 6.9)	1.06 (d, 7.3)	1.05 (d, 7.1)
3-COCH <sub>3</sub>			2.09 (s)
15-COCH <sub>3</sub>			2.07 (s)
28-COCH <sub>3</sub>			2.06 (s)

<sup>a</sup> Measured at 600 MHz. <sup>b</sup> Measured at 500 MHz, in pyridine-*d*<sub>5</sub>.

Hz, H $\beta$ -15), 4.39 (d,  $J$  = 4.3 Hz, H $\beta$ -16), 6.52 (d,  $J$  = 10.1 Hz, H $\alpha$ -21), and 6.21 (d,  $J$  = 10.1 Hz, H $\beta$ -22) in the  $^1\text{H}$  NMR spectrum of **2** confirmed the placement of these four oxygenated carbons at C-15, C-16, C-21, and C-22. The oxymethylene protons of **2** resonated at  $\delta$  3.77 (d,  $J$  = 10.7 Hz) and 3.49 (d,  $J$  = 10.7 Hz), which were deshielded to  $\delta$  4.32 (d,  $J$  = 11.3 Hz) and 4.19 (d,  $J$  = 11.3 Hz) in its triacetate, **2a**.

The two acyl groups were located at C-21 and C-22 on the basis of the fact that in the  $^1\text{H}$  NMR spectrum of the triacetate **2a**, H-21 and H-22 showed two pairs of doublets at  $\delta$  6.42 and 5.87, respectively, whereas in the R<sub>1</sub>-barrigenol pentaacetate, the two pairs of doublets were shifted to  $\delta$  5.66 (H-21) and 5.37 (H-22).<sup>21</sup> This was also evident from the cross-peaks between H-21 ( $\delta$  6.52 d,  $J$  = 10.1 Hz) and the carbonyl carbon of the acetyl moiety ( $\delta$  170.9), C-29 ( $\delta$  29.5), and C-30 ( $\delta$  20.2) and between H-22 ( $\delta$  6.21, d,  $J$  = 10.1 Hz) and the carbonyl carbon of the 2-methylbutyryl moiety ( $\delta$  176.6) and C-16 ( $\delta$  73.1) in its HMBC spectrum. The protons attached to carbons bearing acetyl groups at C-15, C-3, and C-28 were observed at  $\delta$  5.40 (d,  $J$  = 4.2 Hz), 4.71 (dd,  $J$  = 4.9, 11.7 Hz), and 4.32 (d,  $J$  = 11.3 Hz), 4.12 (d,  $J$  = 11.3 Hz), respectively, and at  $\delta$  4.22 (d,  $J$  = 4.3 Hz), 3.47 (dd,  $J$  = 5.3, 10.7 Hz), and 3.77 (d,  $J$  = 10.7 Hz), 3.49 (d,  $J$  = 10.7 Hz), respectively, in **2** (Table 1).

The relative configuration at various stereogenic centers was deduced on the basis of NOESY experiments of **2** and **2a** (Table 3, Figure 2). From the aforementioned data compound **2** was identified as 21 $\alpha$ -acetoxo-3 $\beta$ ,15 $\alpha$ ,16 $\alpha$ ,22 $\alpha$ -tetrahydroxy-21 $\beta$ -(2-methylbutyryl)olean-12-ene. A literature survey revealed that **2**

**Table 2.**  $^{13}\text{C}$  NMR Data for Compounds **1**, **2**, and **2a**

carbon no.	<b>1</b> <sup>a</sup>	<b>2</b> <sup>b</sup>	<b>2a</b> <sup>a</sup>
1	36.6	37.0	37.3
2	28.0	28.4	29.4
3	77.9	78.0	80.52
4	39.2	39.5	38.7
5	55.5	55.8	55.1
6	19.0	19.3	19.1
7	39.1	39.4	38.0
8	41.3	41.6	41.7
9	47.2	47.4	47.2
10	37.2	37.5	38.0
11	24.0	24.2	24.2
12	125.6	125.4	127.0
13	143.2	143.6	141.3
14	47.8	47.9	47.3
15	67.4	67.7	72.0
16	72.5	73.1	69.3
17	46.2	48.6	47.3
18	42.0	41.0	42.2
19	46.9	46.9	47.1
20	36.9	36.4	36.4
21	76.1	79.4	78.6
22	77.6	73.2	73.8
23	28.5	28.9	28.3
24	15.8	17.1	17.2
25	16.5	16.1	15.9
26	17.6	17.8	17.9
27	21.0	21.2	21.7
28	67.0	63.1	66.8
29	30.0	29.5	29.4
30	19.1	20.2	20.2
21-COCH <sub>3</sub>		170.9	170.9
21-COCH <sub>3</sub>		21.3	21.4
22-COCH <sub>3</sub>	170.9		
22-COCH <sub>3</sub>	20.9		
1'	176.0	176.6	176.0
1'	41.6	41.6	41.8
3'	26.9	27.0	27.0
4'	11.6	12.1	12.2
5'	16.6	17.8	17.2
3-COCH <sub>3</sub>			170.9
3-COCH <sub>3</sub>			21.4
15-COCH <sub>3</sub>			171.2
15-COCH <sub>3</sub>			21.8
28-COCH <sub>3</sub>			170.9
28-COCH <sub>3</sub>			22.0

<sup>a</sup> Measured at 150 MHz. <sup>b</sup> Measured at 125 MHz, in pyridine-*d*<sub>5</sub>.

is the 3-*O*-aglycone of hacquetiasaponin **6**, previously isolated from *Hacquetia epipactis*.<sup>22</sup> The physical data of the aglycone **6** were not published. Thus, this is the first report of the isolation of this aglycone from the fruits of *B. racemosa*.

The cytotoxicity of compounds **1**–**5** was tested against HeLa and P388D1 carcinoma cell lines using the MTT assay. However, none of these compounds had statistically significant cytotoxicity (IC<sub>50</sub> > 50  $\mu\text{M}$ ) for all the cell lines tested.

## Experimental Section

**General Experimental Procedures.** Optical rotations were determined on Perkin-Elmer polarimeter. IR spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer with KBr pellets.  $^1\text{H}$  NMR (500 and 600 MHz) and  $^{13}\text{C}$  NMR (125 and 150 MHz) spectra were recorded on a Varian XL-300, a Varian INOVA-500, or a GE NMR Omega 600 spectrometer in C<sub>5</sub>D<sub>5</sub>N with TMS as internal standard. Coupling constants ( $J$ ) are given in Hz. MS were obtained with a JEOL MS-BU 20 or a JEOL LMS-SX-120A QQ mass spectrometer. Column chromatography was performed with silica gel (100–200, 230–400 mesh, Acme). Silica gel 60 F254 (0.25 mm, Merck) was used for analytical TLC.

**Plant Material.** Dried fruits of *B. racemosa* were procured from a local market in Trivandrum (State of Kerala), India, and were authenticated by Prof. M. Venkaiah, Department of Botany, Andhra University, Visakhapatnam. A voucher specimen (No. IIC-MG-100)

**Table 3.** HMBC, COSY, and NOESY Data for Compounds **1**, **2**, and **2a**

proton no.	<b>1</b>			<b>2</b>			<b>2a</b>		
	HMBC	COSY	NOESY	HMBC	COSY	NOESY	HMBC	COSY	NOESY
1 $\alpha$	2, 3, 5, 9, 10, 23		9						
1 $\beta$			26						
2		3 $\alpha$	3 $\alpha$ , 23		3 $\alpha$	3 $\alpha$ , 23		3 $\alpha$	3 $\alpha$ , 23
3 $\alpha$	4, 23, 24	2	2, 5 $\alpha$ , 23	4, 23, 24	2	2, 23	4, 23, 24, <u>COCH<sub>3</sub></u>	2	2, 23
5 $\alpha$			3 $\alpha$						
6									
7									
9 $\alpha$	8, 10, 11								
11			26						
12			19	11		19	11		19
15	14, 27	16	16, 26	14, 27	16	16, 26	<u>COCH<sub>3</sub></u> , 14, 27	16	16, 26
16	14, 15, 17, 18, 22	15	15	14, 15, 17, 18, 22	15	15, 28b	14, 15, 17, 18, 22	15	15, 28b
18	12, 13, 16, 17, 28	19	15	17	19		17	19	
19	13, 20, 21, 29	18	12, 29	29	18	12	29	18	12
21	20, 22, 29, 30	22	29	<u>COCH<sub>3</sub></u> , 20, 22, 29, 30	22	29	<u>COCH<sub>3</sub></u> , 20, 22, 29, 30	22	29
22	<u>COCH<sub>3</sub></u> , 16, 17, 21, 28	21	28a, 28b, 30	1', 16, 17, 21, 28	21	30	1', 16, 17, 21, 28	21	30
23	3, 4, 5, 24			3, 4, 5, 24			3, 4, 5, 24		
24	3, 4, 5, 25			3, 4, 5, 25			3, 4, 5, 25		
25	1, 5, 9, 10			1, 5, 9, 10			1, 5, 9, 10		
26	7, 8, 9, 14	15		7, 8, 9, 14		15	7, 8, 9, 14		
27	8, 13, 14, 15			8, 13, 14, 15			8, 13, 14, 15		
28a	1', 16, 17, 18, 22	15, 28b		16, 17, 18, 22	28b	18	16, 17, 18, 22	28b	
28b		28a			28a	18		28a	
29	19, 20, 21, 30		21	19, 20, 21, 30		21	19, 20, 21, 30		21
30	19, 20, 21, 29		22	19, 20, 21, 29		22	19, 20, 21, 29		22
21-O-COCH <sub>3</sub>				<u>COCH<sub>3</sub></u>			<u>COCH<sub>3</sub></u>		
22-O-COCH <sub>3</sub>	<u>COCH<sub>3</sub></u>		5', 3' a				1'		
2'	1', 3', 4', 5'	7'		1', 3', 4', 5'	7'		1', 3', 4', 5'	7'	
3'	1', 2', 4', 5'			1', 2', 4', 5'			1', 2', 4', 5'		
4'	2', 3'			2', 3'			2', 3'		
5'	1', 2', 3'	2'		1', 2', 3'	2'		1', 2', 3'	2'	
3, 15, 28-OCOCH <sub>3</sub>									

is preserved in the Organic Division-1, Indian Institute of Chemical Technology, Hyderabad, India.

**Extraction and Isolation.** The dried fruits of *B. racemosa* (1.2 kg) were extracted three times (each for seven days) with MeOH at room temperature. The filtrate was concentrated to yield a MeOH extract (40 g). A portion (30 g) of this brown syrup was subjected to column chromatography over silica gel using solvent mixtures of increasing polarity from CHCl<sub>3</sub> through MeOH to give several fractions. Fraction 1 (500 mg) was chromatographed on silica gel with CHCl<sub>3</sub> to afford stigmaterol (**3**) (40 mg), with 1% MeOH to yield racemosol A (**1**) (15 mg), and with 2% MeOH to furnish isoracemosol A (**2**) (10 mg). Fraction 2 (200 mg) was subjected to silica gel CC using 3% MeOH to afford barringtonenol C (**4**) (7 mg) and 5% MeOH to yield bartogenic acid (**5**) (10 mg).

**Racemosol A (1):** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>27</sup> +7 (c 1.0, MeOH); IR (KBr)  $\nu_{\max}$  3426, 1738, 1709, 1648, 1462, 1243, 1193, 1043 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data, see Tables 1 and 2; 2D NMR, see Figures 1 and 2, Table 3; HRESIMS *m/z* 655.4157 [M + Na]<sup>+</sup> (calcd for C<sub>30</sub>H<sub>60</sub>O<sub>8</sub>Na, 655.4180).

**Alkaline Hydrolysis of 1.** Compound **1** (5 mg) was refluxed for 3 h in a solution of 3% KOH (2 mL). The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and the organic phase was washed with H<sub>2</sub>O and evaporated to yield **1a** (2 mg).

**Compound 1a:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>27</sup> +38 (c 1.0, MeOH).

**Isoracemosol A (2):** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>27</sup> +25 (c 1.0, MeOH); IR (KBr)  $\nu_{\max}$  3445, 1743, 1708, 1646, 1463, 1238, 1193, 1073 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data, see Tables 1 and 2; 2D NMR, see Figures 1 and 2, Table 3; HRESIMS *m/z* 655.4224 [M + Na]<sup>+</sup> (calcd for C<sub>37</sub>H<sub>60</sub>O<sub>8</sub>Na, 655.4180).

**3 $\beta$ ,15 $\alpha$ ,28-Triacetoxisoracemosol A (2a):** white, amorphous powder; IR (KBr)  $\nu_{\max}$  3486, 1739, 1462, 1243, 1147, 1029 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data, see Tables 1 and 2; 2D NMR, see Table 3.

**Barringtonenol C (4):** white, amorphous powder; mp 276–278 °C; [ $\alpha$ ]<sub>D</sub><sup>27</sup> +15 (c 1.0, MeOH); IR (KBr)  $\nu_{\max}$  3422, 2923, 2853, 1632, 760 cm<sup>-1</sup>; ESIMS *m/z* 491 [M + H]<sup>+</sup>.

**Bartogenic acid (5):** white, amorphous powder; mp 315–16 °C; [ $\alpha$ ]<sub>D</sub><sup>27</sup> +116 (c 1.0, MeOH); IR (KBr)  $\nu_{\max}$  3445, 2943, 1694, 1458, 1386, 1263, 1066, cm<sup>-1</sup>; ESIMS *m/z* 541 [M + Na]<sup>+</sup>.

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**Supporting Information Available:** This material is available free of charge via the Internet at <http://pubs.acs.org>.

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