

# Triterpenoids from *Tillandsia fasciculata*

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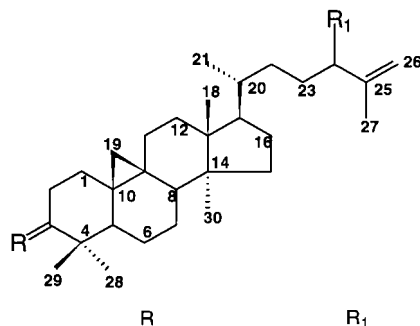
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The leaves of *Tillandsia fasciculata* afforded four tetracyclic triterpenoids of the cycloartane type, two new compounds identified as cyclolaudenyl formate (**2**) and the (24*S*)-24-isopropenyl cycloartanone, which we named tillandsinone (**1**), and the known cyclolaudenone (**3**) and cyclolaudenol (**4**).

The genus *Tillandsia* is an interesting group of epiphytic plants with about 500 species, which belong to the subfamily Tillandsioideae of the family Bromeliaceae. There are about 175 species recorded in México, 20 of which can be found in the state of Yucatán.<sup>1,2</sup> A search of the literature showed very few *Tillandsia* species chemically studied. *Tillandsia usneoides*, commonly known as "Spanish moss", is the most extensively studied, followed by *Tillandsia recurvata*. The studied species contain cycloartane triterpenoids, pentacyclic triterpenes, sterols,<sup>3,4</sup> and flavonoids.<sup>5,6</sup>

As part of our search for biologically active compounds of plants from the ecological reserve "El Eden" located in the state of Quintana Roo in México, we have undertaken the phytochemical study of *Tillandsia fasciculata* Swartz (Bromeliaceae), which is one of the more abundant species in the area. Column chromatography of the hexane and dichloromethane extracts of dried leaves of *T. fasciculata* afforded four cycloartane triterpenoids (**1–4**).



|          | R           | R <sub>1</sub> |
|----------|-------------|----------------|
| <b>1</b> | =O          | β-iPr          |
| <b>2</b> | β-OCOH, α-H | Me             |
| <b>3</b> | =O          | Me             |
| <b>4</b> | β-OH, α-H   | Me             |
| <b>5</b> | β-OAc, α-H  | Me             |

The <sup>1</sup>H NMR spectra of compounds **1–4** (Table 1) indicated the presence of a cycloartane type skeleton with the typical high-field AB doublets due to the nonequivalent hydrogens (H-19) of the 9β,19 cyclopropane ring.<sup>3</sup>

**Table 1.** <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (75 MHz) Spectral Data for Tillandsinone (**1**) and Cyclolaudenyl Formate (**2**) in CDCl<sub>3</sub>

| position | <b>1</b>                        |                      | <b>2</b>                        |                      |
|----------|---------------------------------|----------------------|---------------------------------|----------------------|
|          | δ <sub>H</sub> (ppm),<br>J (Hz) | δ <sub>C</sub> (ppm) | δ <sub>H</sub> (ppm),<br>J (Hz) | δ <sub>C</sub> (ppm) |
| 1α       | 1.85 tdd (13.5, 4.5, 1.0)       | 33.4 t               | 1.60 m                          | 31.5 t               |
| 1β       | 1.54 m <sup>a</sup>             |                      | 1.25 m                          |                      |
| 2α       | 2.30 ddd (14, 4.5, 3.0)         | 37.5 t               | 1.75 m                          | 26.9 t               |
| 2β       | 2.71 td (14.0, 5.0, 7.0)        |                      | 1.60 m                          |                      |
| 3        |                                 | 216.6 s              | 4.57 dd (11.5, 4.5)             | 80.3 d               |
| 4        |                                 | 50.3 s               |                                 | 39.4 s               |
| 5        | 1.71 dd (12.5, 4.5)             | 48.5 d               | 1.40 m                          | 47.2 d               |
| 6α,6β    | 1.55 m, 0.94 m                  | 21.5 t               | 1.60 m, 0.80 m                  | 20.9 t               |
| 7α,7β    | 1.28 m, 1.90 m                  | 28.1 t               | 1.27 m, 1.86 m                  | 28.0 t               |
| 8        | 1.58 m                          | 47.9 d               | 1.50 m                          | 47.8 d               |
| 9        |                                 | 21.1 s               |                                 | 20.1 s               |
| 10       |                                 | 25.9 s               |                                 | 25.8 s               |
| 11α,11β  | 2.03 m, 1.17 m                  | 26.8 t               | 1.98 m, 1.11 m                  | 26.5 t               |
| 12       | 1.65 m (2H)                     | 32.8 t               | 1.60 m (2H)                     | 32.8 t               |
| 13       |                                 | 48.7 s               |                                 | 48.8 s               |
| 14       |                                 | 45.3 s               |                                 | 45.2 s               |
| 15       | 1.28 m (2H)                     | 35.6 t               | 1.27 m (2H)                     | 35.5 t               |
| 16       | 1.38 m, 1.14 m                  | 25.9 t               | 1.32 m, 1.12 m                  | 25.8 t               |
| 17       | 1.60 m                          | 52.2 d               | 1.57 m                          | 52.2 d               |
| 18       | 0.98 s                          | 18.0 q               | 0.96 s                          | 17.9 q               |
| 19α      | 0.57 d (4.5)                    | 29.6 t               | 0.35 d (4.4)                    | 29.7 t               |
| 19β      | 0.79 d (4.0)                    |                      | 0.59 d (4.4)                    |                      |
| 20       | 1.32 m                          | 36.7 d               | 1.35 m                          | 36.0 d               |
| 21       | 0.88 d (7.0)                    | 18.7 q               | 0.86 d (6.5)                    | 18.3 q               |
| 22       | 0.80 m, 1.37 m                  | 34.5 t               | 0.93 m, 1.32 m                  | 33.9 t               |
| 23       | 1.03 m, 1.62 m                  | 26.8 t               | 1.14 m, 1.45 m                  | 31.6 t               |
| 24       | 1.53 m                          | 55.5 d               | 2.09 m <sup>b</sup>             | 41.6 d               |
| 25       |                                 | 147.4 s              |                                 | 150.2 s              |
| 26a      | 4.61 da (2.5)                   | 111.9 t              | 4.66 m                          | 109.3 t              |
| 26b      | 4.75 dq (2.5, 1.5)              |                      | 4.67 m                          |                      |
| 27       | 1.58 s (br)                     | 19.0 q               | 1.69 s (br)                     | 18.6 q               |
| 28       | 1.05 s                          | 22.2 q               | 0.89 s                          | 25.3 q               |
| 29       | 1.10 s                          | 20.8 q               | 0.91 s                          | 15.1 q               |
| 30       | 0.90 s                          | 19.3 q               | 0.89 s                          | 19.3 q               |
| 31       | 1.52                            | 30.3 d               | 1.00 d (6.9)                    | 20.1 q               |
| 32       | 0.92 d (6.0)                    | 20.8 q               |                                 |                      |
| 33       | 0.81 d (6.0)                    | 21.5 q               |                                 |                      |
| H-COO-   |                                 |                      | 8.12 s                          | 161.1 d              |

<sup>a</sup> Assignments and chemical shifts of overlapped <sup>1</sup>H multiplets are based on COSY, NOESY, and HMQC experiments; <sup>13</sup>C assignments confirmed by DEPT, HMQC, and HMBC experiments. <sup>b</sup> Pseudo-sextet (*J* ≈ 7.0 Hz).

Compound **1** gave a molecular ion peak (HRMS) corresponding to the molecular formula C<sub>33</sub>H<sub>54</sub>O. Chemical

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shifts of the proton and carbon signals of the C-19 methylene group and the C-18, C-28, C-29, and C-30 tertiary methyl groups were almost identical with those of cyclolaudenone (**3**), and the presence of a carbonyl signal at  $\delta$  216.6 suggested that **1** had the same cycloartane nucleus. Fragment peaks at  $m/z$  355, 341, 313, and 175 in the mass spectra of both compounds **1** and **3** supported the above assumption. The major fragment ions at  $m/z$  313 ( $M - C_{11}H_{21}$ )<sup>+</sup>, 328 ( $M - C_9H_{14}O$ )<sup>+</sup>, 175 [ $M - C_{11}H_{21} - C_9H_{14}O$  (ring A)]<sup>+</sup> indicated that compound **1** was a cycloartane-type triterpene with a  $C_{11}$  side chain. The ions at  $m/z$  328 and 175 corresponding to the loss of ring A were characteristic of 9 $\beta$ ,19-cyclotetracyclic triterpenes.<sup>7</sup>

The <sup>1</sup>H NMR spectrum (Table 1) showed differences compared with that of cyclolaudenone (**3**), at the chemical shifts of the C-26 terminal methylene protons and the C-24 methine group. The methylene protons appeared in **1** as a broad doublet at  $\delta$  4.61 ( $J = 2.5$  Hz) and a doublet of quartets at  $\delta$  4.75 ( $J = 2.5$  and 1.5 Hz), similar to the 24-ethyl compound cyclomargenone,<sup>8</sup> and the H-24 signal was shifted upfield from  $\delta$  2.10 in cyclolaudenone (**3**) to  $\delta$  1.53 in tillandsinone (**1**). The <sup>13</sup>C NMR spectrum of **1** (Table 1) showed two extra carbon signals, one for a secondary methyl and one for a methine group. Differences in the MS and <sup>1</sup>H and <sup>13</sup>C NMR can be explained assuming the presence of an isopropyl group at C-24 in **1** instead of the methyl group in **3**. This assumption was also in accordance with the downfield shift of C-24 (from  $\delta$  41.6 to 55.5,  $\beta$  effect) and the upfield shifts of C-23 and C-25 (from  $\delta$  31.4 and 150.2 to  $\delta$  26.8 and 147.4, respectively) due to the  $\gamma$  effect of the two methyl groups. HMBC experiments confirmed the presence of the isopropyl group at C-24, since long-range couplings were observed between the C-24 ( $\delta$  55.5) and the protons of the vinyl methyl (H-27,  $\delta$  1.58), the terminal methylene (H-26,  $\delta$  4.61 and 4.75), and the secondary methyl groups (H-32 and H-33,  $\delta$  0.92 and 0.81). Thus, tillandsinone was identified as 24-isopropenylcycloartan-3-one (**1**).

Triterpenes and sterols having nonconventional side chains, as in tillandsinone (**1**), are rare in terrestrial plants, and they have so far been detected only in *Nervilia purpurea* (Orchidaceae)<sup>9</sup> and *Viola formosana* (Violaceae).<sup>10</sup> Sterols with this type of side chain alkylation pattern are more common in marine sponges; they have been reported from *Aplysina* species,<sup>11</sup> *Pseudaxinyssa* sp.,<sup>12</sup> and *Dysidea herbacea*.<sup>13</sup> The stereochemistry of the side chain of 24-isopropenylcholesterol and cyclohomonervilol, a triterpenoid with the same type of side chain, was established by chemical correlation with clionasterol<sup>9</sup> and 24*S*-dihydrocyclofuntumienol.<sup>14</sup> Careful examination and comparison of the published <sup>1</sup>H NMR and <sup>13</sup>C NMR data<sup>15</sup> with those of tillandsinone (**1**) showed these to be very similar (Table 1). Therefore tillandsinone must be (24*S*)-24-isopropenylcycloartan-3-one (**1**).

The HREIMS spectrum of compound **2** showed a molecular formula of  $C_{32}H_{52}O_2$ . The <sup>13</sup>C NMR spectrum (Table 1) showed signals for 32 carbon atoms, which accounted for seven methyl groups, 12 methylenes, seven methines, and six tetrasubstituted carbons (DEPT). The <sup>1</sup>H NMR spectrum was similar to that of cyclolaudenyl acetate (**5**), but it lacked the acetate methyl signal. Another significant difference with **5** was the presence of a low-field singlet at  $\delta$  8.1, which showed a cross-peak with a doublet signal at  $\delta$  161.1 in the HMQC experiment and with the methine carbon signal at 80.3 in the HMBC experiment. These <sup>1</sup>H and <sup>13</sup>C differences indicated a formate group at C-3 in compound **2**, instead of an acetate, as in compound **5**. The

mass spectral data were in agreement with the above assumption since the MS showed the same significant fragment peaks as cyclolaudenol (**4**) and its corresponding acetate **5**. On the basis of all the above data, compound **2** was identified as cyclolaudenyl formate.

The known compounds were identified as cyclolaudenone (**3**) and cyclolaudenol (**4**), by comparison of their <sup>1</sup>H NMR and MS spectral data with those reported in the literature.<sup>8,16,17</sup> Although **3** and **4** are known compounds isolated from various plant species, complete NMR assignments were not found in the literature. Some of the published data for cyclolaudenol (**4**) and its acetate (**5**) are confusing, as those reported by Govardan<sup>16</sup> and Desoki<sup>17</sup> differ from those reported by Ageta.<sup>8</sup> <sup>1</sup>H and <sup>13</sup>C NMR assignments for compounds **3**, **4**, and **5** were based on 1D and 2D NMR experiments, including DEPT, COSY, HMQC, and HMBC experiments.

## Experimental Section

**General Experimental Procedures.** Melting points were determined on a Fisher-Jones type apparatus and are uncorrected. Optical rotations were measured in CHCl<sub>3</sub> solutions on a Jasco DIP 360 polarimeter. IR spectra were recorded on KBr disks on a Nicolet Magna Fourier transform IR spectrometer 550. EIMS were obtained on a Hewlett-Packard 5892 mass spectrometer using a Hewlett-Packard 5970 series II gas chromatograph as injection system. HREIMS were done on a VG Micromass LTD-ZAB-2F spectrometer at 70 eV. NMR spectra were recorded on Varian Unity PLUS 500 and Bruker Advance 400 spectrometers in CDCl<sub>3</sub> solutions with TMS as internal standard; chemical shifts are recorded in  $\delta$  values.

**Plant Material.** *Tillandsia fasciculata* was collected at "El Eden" ecological reserve located at 21° 3' N, 87° 11' W of Cancún Q. R. (México) in January 1999 and authenticated by Gillian Schultz. A voucher specimen has been deposited at the herbarium Alfredo Barrera Marín, Universidad Autónoma de Yucatán, Mérida, México.

**Extraction and Isolation.** Dried and ground leaves of *T. fasciculata* (1.0 kg) were extracted at room temperature by percolation with hexane, CH<sub>2</sub>Cl<sub>2</sub>, and MeOH to give green dark residues (ca. 11, 10, and 38 g, respectively). The hexane residue (8.3 g) was chromatographed on a column of silica gel (4.5  $\times$  15.0 cm), eluted with hexane, mixtures of hexane-CH<sub>2</sub>Cl<sub>2</sub> (8:2, 6:4, 4:6), CH<sub>2</sub>Cl<sub>2</sub>, mixtures of CH<sub>2</sub>Cl<sub>2</sub>-EtOAc (9:1, 8:2, 6:4), and EtOAc. Eluates (84) were collected, monitored by TLC, and combined in four major fractions (A-D). Fraction A was identified by GC-MS as a mixture of C<sub>27</sub> to C<sub>33</sub> hydrocarbons. Fraction B treated with acetone gave 206.9 mg of precipitate, which was chromatographed on silica gel (15 g) using hexanes-EtOAc as eluent. Fractions 1 and 2 contained a mixture of cyclolaudenone (**3**)<sup>8</sup> and tillandsinone (**1**), which were further separated by TLC on 10% AgNO<sub>3</sub>-silica gel with hexane-CH<sub>2</sub>Cl<sub>2</sub> (8:2, developed 2 $\times$ ), giving 23.4 mg of **1** and 9.6 mg of **3**. Fraction C (4.71 g) was chromatographed over silica gel with CH<sub>2</sub>Cl<sub>2</sub> as eluent. Fractions 3-5 were combined with fractions 3 and 4 from the chromatography of the CH<sub>2</sub>Cl<sub>2</sub> extract and separated in acidic and neutral compounds, using a 5% solution of NaOH. The neutral fraction (292.4 mg) was repeatedly subjected to CC over ordinary silica gel and 10% AgNO<sub>3</sub>-silica gel to afford 2.8 mg of cyclolaudenyl formate (**2**), 5 mg of **1**, and 20.5 mg of a mixture of **3** and **1**. Fractions 6-14 (457 mg) treated in the same way afforded 6.5 mg of cyclolaudenol (**4**).<sup>8</sup> Fraction D (210.5 mg) gave a mixture of sterols identified by GC-MS as  $\beta$ -sitosterol, stigmasterol, and campesterol.

**Tillandsinone (1):** colorless fine needles, mp 125 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +26.6° (c 0.18, CHCl<sub>3</sub>); IR (KBr)  $\nu_{max}$  3072, 1699, 884 cm<sup>-1</sup>; EIMS  $m/z$  466 [M]<sup>+</sup> (88), 451 [M - Me]<sup>+</sup> (18), 368 [M - C<sub>7</sub>H<sub>13</sub> - H]<sup>+</sup> (12), 355 [M - C<sub>8</sub>H<sub>15</sub>]<sup>+</sup> (9), 341 [M - C<sub>9</sub>H<sub>17</sub>]<sup>+</sup> (7), 328 [M - (ring A + H)]<sup>+</sup> (13), 313 [M - SC (C<sub>11</sub>H<sub>21</sub>)]<sup>+</sup> (69), 175 [M - (ring A + H) - SC (C<sub>11</sub>H<sub>21</sub>)]<sup>+</sup> (38); <sup>1</sup>H and <sup>13</sup>C NMR (see Table 1); HREIMS  $m/z$  466.4166 [M]<sup>+</sup> (calcd for C<sub>33</sub>H<sub>54</sub>O, 466.4174).

**Cyclolaudenyl formate (2):** colorless gum; EIMS  $m/z$  468  $[M]^+$  (22), 453  $[M - Me]^+$  (17), 422  $[M - HCO_2H]^+$  (40), 407  $[M - HCO_2H - Me]^+$  (36), 379  $[M - HCO_2H - C_3H_7]^+$  (9), 353  $[M - HCO_2H - C_5H_9]^+$  (10), 300  $[M - (ring A+H)]^+$  (31), 297  $[M - HCO_2H - SC(C_9H_{17})]^+$  (24), 203  $[M - (ring A+H) - C_7H_{13}]^+$  (40), 175  $[M - (ring A+H) - SC(C_9H_{17})]^+$  (49);  $^1H$  and  $^{13}C$  NMR (see Table 1); HREIMS  $m/z$  468.3994  $[M]^+$  (calcd for  $C_{32}H_{52}O_2$ , 468.3967).

**Cyclolaudenone (3):**  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  4.67 (2H, m, H-26), 2.70 (1H, td,  $J = 14.0, 6.5$  Hz, H-2 $\beta$ ), 2.30 (1H, ddd,  $J = 14.0, 4.5, 2.5$  Hz, H-2 $\alpha$ ), 2.10 (1H, pseudo sextet,  $J \sim 7.0$  Hz, H-24), 2.04 (1H, m, H-11 $\alpha$ ), 1.90 (1H, m, H-11 $\beta$ ), 1.86 (1H, tdd,  $J = 13.5, 4.0, 1.0$  Hz, H-1 $\alpha$ ), 1.70 (1H, dd,  $J = 12.5, 4.5$  Hz, H-5), 1.65 (2H, m, H-12), 1.64 (3H, brs, H-27), 1.58 (1H, m, H-17), 1.58 (1H, dd,  $J = 12.5, 5.0$ , H-8), 1.56 (m, H-6 $\alpha$ ), 1.44 (m, H-23a), 1.38 (m, H-16a), 1.35 (m, H-22a), 1.30 (2H, m, H-15), 1.28 (m, H-7 $\beta$ ), 1.15 (m, H-16b, H-11 $\beta$ ), 1.14 (m, H-23b), 1.10 (3H, s, H-29), 1.05 (3H, s, H-28), 1.00 (3H, d,  $J = 7$  Hz), 0.99 (3H, s, H-18), 0.95 (m, H-6 $\beta$ ), 0.94 (m, H-22b), 0.90 (3H, s, H-30), 0.87 (3H, d,  $J = 6.5$  Hz, H-21), 0.78, 0.56 (each 1H, d,  $J = 4.5$  Hz, H-19);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  216.6 (s, C-3), 150.2 (s, C-25), 109.4 (t, C-26), 52.3 (d, C-17), 50.2 (s, C-4), 48.7 (s, C-13), 48.4 (d, C-5), 47.9 (d, C-8), 45.3 (s, C-14), 41.6 (d, C-24), 37.5 (t, C-2), 36.0 (d, C-20), 35.6 (t, C-15), 33.9 (t, C-22), 33.4 (t, C-1), 32.8 (t, C-12), 31.5 (t, C-23), 29.6 (t, C-19), 28.1 (t, C-7), 26.8 (t, C-11), 26.0 (s, C-10), 25.9 (t, C-16), 22.2 (q, C-28), 21.5 (t, C-6), 21.1 (s, C-9), 20.8 (q, C-29), 20.1 (q, C-31), 19.3 (q, C-30), 18.7 (q, C-27), 18.3 (q, C-21), 18.0 (q, C-18).

**Cyclolaudenol (4):**  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  4.67 (2H, m, H-26), 3.28 (1H, dd,  $J = 11.5, 4.5$  Hz, H-3), 2.10 (1H, pseudo sextet,  $J \sim 7.0$  Hz, H-24), 1.96 (1H, m, H-11 $\alpha$ ), 1.87 (1H, m, H-7 $\beta$ ), 1.75 (1H, m, H-2 $\alpha$ ), 1.64 (3H, brs, H-27), 1.60 (2H, m, H-12), 1.58 (1H, m, H-6 $\alpha$ ), 1.56 (m, H-1 $\alpha$ , H-2 $\beta$ , H-17), 1.50 (1H, m, H-8), 1.42 (1H, m, H-23a), 1.36 (1H, m, H-20), 1.33 (2H, m, H-16a, H-22a), 1.28 (4H, m, H-5, H-7 $\alpha$ , H-15a,b), 1.24 (1H, m, H-1 $\beta$ ), 1.10 (H, m, H-11 $\beta$ , H-16b, H-23a), 1.00 (3H, d,  $J = 7.0$  Hz, H-31), 0.97 (3H, s, H-28), 0.96 (3H, s, H-18), 0.92 (H, m, H-22b), 0.89 (3H, s, H-30), 0.86 (3H, d,  $J = 6.5$  Hz, H-21), 0.81 (3H, s, H-29), 0.80 (1H, m, H-6 $\beta$ ), 0.55, 0.33 (each 1H, d,  $J = 4.5$  Hz, H-19);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  150.2 (s, C-25), 109.4 (t, C-26), 78.9 (d, C-3), 52.3 (d, C-17), 48.8 (s, C-13), 48.0 (d, C-8), 47.1 (d, C-5), 45.3 (s, C-14), 41.6 (d, C-24), 40.5 (s, C-4), 36.0 (d, C-20), 35.6 (t, C-15), 33.9 (t, C-22), 32.9 (t, C-12), 32.0 (t, C-1), 31.5 (t, C-23), 30.4 (t, C-2), 29.9 (t, C-19), 28.1 (t, C-7), 26.5 (t, C-11), 26.1 (s, C-10), 26.0 (t, C-16), 25.4 (q, C-28), 21.1 (t, C-6), 20.1 (q, C-31), 20.0 (s, C-9), 19.3 (q, C-30), 18.7 (q, C-27), 18.3 (q, C-21), 18.0 (q, C-18), 14.0 (q, C-29).

**Cyclolaudenyl Acetate (5):** Crude cyclolaudenol (4, 19.2 mg) was acetylated in the usual manner, and the reaction mixture purified on a column of 10%  $AgNO_3$ -silica gel, to give 3.3 mg of cyclolaudenyl acetate (5);  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  4.67 (2H, m, H-26), 4.57 (1H, dd,  $J = 11.0, 4.5$  Hz, H-3),

2.09 (1H, pseudo sextet,  $J \sim 7.0$  Hz, H-24), 2.0 (1H, m, H-11 $\alpha$ ), 1.84 (1H, m, H-7 $\beta$ ), 1.74 (1H, m, H-2 $\alpha$ ), 1.64 (3H, brs, H-27), 1.60 (2H, m, H-12), 1.60 (1H, m, H-6 $\alpha$ ), 1.58 (m, H-2 $\beta$ , H-17), 1.56 (H, m, H-1 $\alpha$ ), 1.50 (1H, m, H-8), 1.48 (1H, m, H-23a), 1.40 (1H, m, H-5), 1.38 (1H, m, H-20), 1.34 (1H, m, H-16a), 1.32 (1H, m, H-22a), 1.28 (2H, m, H-15a,b), 1.24 (2H, m, H-1 $\beta$ , H-7 $\alpha$ ), 1.12 (1H, m, H-23a), 1.10 (1H, m, H-16b), 1.08 (H, m, H-11 $\beta$ ), 1.00 (3H, d,  $J = 7.0$  Hz, H-31), 0.98 (H, m, H-22b), 0.95 (3H, s, H-18), 0.89 (6H, s, H-29, H-30), 0.86 (3H, d,  $J = 6.5$  Hz, H-21), 0.85 (3H, s, H-28), 0.82 (1H, m, H-6 $\beta$ ), 0.57, 0.34 (each 1H, d,  $J = 4.5$  Hz, H-19);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  150.3 (s, C-25), 109.4 (t, C-26), 80.7 (d, C-3), 52.2 (d, C-17), 48.8 (s, C-13), 47.8 (d, C-8), 47.2 (d, C-5), 45.3 (s, C-14), 41.6 (d, C-24), 39.4 (s, C-4), 36.0 (d, C-20), 35.5 (t, C-15), 33.9 (t, C-22), 32.8 (t, C-12), 31.5 (t, C-1), 31.5 (t, C-23), 29.7 (t, C-19), 28.1 (t, C-7), 26.8 (t, C-11), 26.5 (t, C-2), 26.0 (s, C-10), 25.8 (t, C-16), 25.4 (q, C-28), 20.9 (t, C-6), 20.1 (q, C-31), 20.1 (s, C-9), 19.3 (q, C-30), 18.7 (q, C-27), 18.3 (q, C-21), 17.9 (q, C-18), 15.1 (q, C-29).

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