

## Pyrrolizidine Alkaloids and Diterpenes from *Villasenorina orcuttii*

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O estudo químico da *Villasenorina orcuttii*, a única espécie do gênero *Villasenorina*, levou ao isolamento de três diterpenos acíclicos, dois deles descritos pela primeira vez. Dois alcaloides pirrolizidínicos, flososenina e floridanina, entre outros compostos já conhecidos, também foram isolados. A configuração absoluta da floridanina foi determinada por análise de raios X usando dispersão anômala com radiação Cu K $\alpha$ , e seus dados de ressonância magnética nuclear (RMN) de <sup>1</sup>H e de <sup>13</sup>C foram corrigidos.

The chemical study of *Villasenorina orcuttii*, the only species of the genus *Villasenorina*, afforded three acyclic diterpenes, two of them described for the first time. Two pyrrolizidine alkaloids, flososenine and floridanine, among other known compounds were also isolated. The absolute configuration of floridanine was determined by X-ray analysis using anomalous dispersion with Cu K $\alpha$  radiation, and its <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) data were corrected.

**Keywords:** *Villasenorina orcuttii*, diterpenes, pyrrolizidine alkaloids, absolute configuration

## Introduction

*Villasenorina orcuttii*, the only species of the genus *Villasenorina* (Asteraceae, Senecioneae), is a shrub that grows in the rainforest of Chiapas, Oaxaca and Southern Veracruz (Mexico) at 100 to 2000 m of elevation.<sup>1</sup> *Villasenorina orcuttii* (formerly *Senecio orcuttii*) was initially included into the genus *Telanthophora*, which together with the genus *Pittocaulon* is constituted by species segregated from the traditional section Terminales Greenm. of the genus *Senecio* s.l.<sup>2</sup> Further studies evidenced the differences between *Senecio* (*Telanthophora orcuttii*) and other species of *Senecio*, *Thelantophora* or *Pittocaulon* and placed it into his own genus: *Villasenorina*.<sup>1</sup> To the best of our knowledge, there is no chemical work on the genus *Villasenorina*. Previous studies on its related genera, *Telanthophora*, *Senecio* and *Pittocaulon*, described

the presence, in the three of them, of sesquiterpene derivatives mainly of eremophilane and/or oplopane types, while pyrrolizidine alkaloids (PAs) have been found only in species of *Senecio* and *Pittocaulon*.<sup>3</sup> As continuation of our survey on Senecioneae, it is reported the isolation of three acyclic diterpenes from *Villasenorina orcuttii*: phytane-1,2,3-triol (**1**), previously obtained as a synthetic product,<sup>4,5</sup> and compounds **2** and **3** which are described for the first time, two PAs: flososenine (**4**)<sup>6-8</sup> and floridanine (**5**),<sup>6,9</sup> together with methyl ferulate (**6**),<sup>10</sup> pterolactame (**7**),<sup>11</sup> tyramine (**8**)<sup>12</sup> and  $\beta$ -sitosteryl glucoside (Figure 1). Additionally, the absolute configuration of floridanine (**5**) was determined by X-ray analysis and its <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) data were corrected.

## Results and Discussion

Compound **2** was obtained as colorless oil. Its IR spectrum indicated the presence of hydroxyl (3455 cm<sup>-1</sup>) and carbonyl

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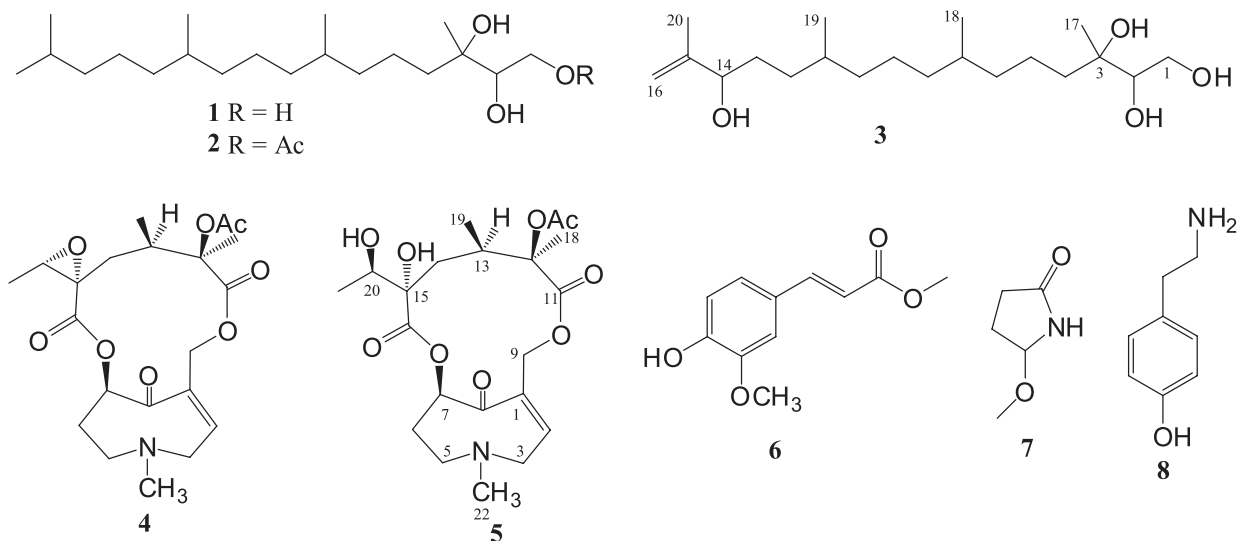


Figure 1. Chemical structures of compounds 1-8.

groups ( $1742\text{ cm}^{-1}$ ). The molecular formula  $\text{C}_{22}\text{H}_{44}\text{O}_4$  was determined by high-resolution electrospray ionization mass spectrometry (HRESIMS). The  $^{13}\text{C}$  NMR analysis of **2** indicated the presence of three oxygenated carbon atoms and a carbonyl function, besides the signals of three methines, nine methylenes and five methyl groups. The  $^1\text{H}$  NMR spectrum exhibited four secondary ( $\delta_{\text{H}} 0.84\text{--}0.88$ ), a tertiary ( $\delta_{\text{H}} 1.23$ ) and an acetyl ( $\delta_{\text{H}} 2.12$ ) methyl groups; an oxygenated methylene ( $\delta_{\text{H}} 4.32$ , dd,  $J 11.6$ ,  $2.8$  Hz;  $4.09$ , dd,  $J 11.6$ ,  $8.4$  Hz) and an oxygenated methine ( $\delta_{\text{H}} 3.69$ , dd,  $J 8.4$ ,  $2.8$  Hz). 2D NMR spectroscopy allowed the identification of a 3,7,11,15-tetramethylhexadecane skeleton with a vicinal terminal triol, one of them acetylated, indicating that compound **2** was the 1-*O*-acetyl derivative of the compound **1**, as confirmed by the isolation of **2** by the selective acetylation of the compound **1**.<sup>13</sup>

Compound **3**, isolated as colorless oil, showed the molecular formula  $\text{C}_{20}\text{H}_{40}\text{O}_4$  (HRESIMS). The NMR spectra were similar to that one from compound **1** with the additional signals of a disubstituted double bond and a hydroxymethine. The long-range (HMBC)  $^1\text{H}$ - $^{13}\text{C}$  NMR correlation experiment allowed to locate these groups at C-15 and C-14, respectively. As in compound **1**, three vicinal hydroxyl groups at C-1, C-2 and C-3 were observed, therefore, the structure of **3** was elucidated as 3,7,11,15-tetramethyl-15-hexadecene-1,2,3,14-tetraol.

The alkaloid **5** was isolated as colorless prisms, mp  $199\text{--}200\text{ }^\circ\text{C}$ . The molecular formula  $\text{C}_{21}\text{H}_{31}\text{NO}_9$  was determined by HRFABMS. The EIMS spectrum showed a molecular ion at  $m/z$  441 and the otonecine-type PAs diagnostic fragment ions<sup>6</sup> at  $m/z$  168 [ $\text{C}_9\text{H}_{14}\text{NO}_2$ ]<sup>+</sup>, 149 [ $\text{C}_9\text{H}_{11}\text{NO}$ ]<sup>+</sup>, 122 [ $\text{C}_7\text{H}_8\text{NO}$ ]<sup>+</sup> and 110 [ $\text{C}_6\text{H}_8\text{NO}$ ]<sup>+</sup>. The presence of the signals of a  $\alpha,\beta$ -unsaturated ketone carbonyl

at  $\delta_{\text{C}} 186.9$  and of three ester carbonyl at  $\delta_{\text{C}} 174.6$ ,  $171.2$  and  $169.9$  in the  $^{13}\text{C}$  NMR spectrum suggested an acetylated macrocyclic diester of otonecine. The proton NMR spectrum of this alkaloid was similar to that of the floridanine,<sup>9</sup> the main difference was the signal of H-20 assigned by the HMBC and COSY correlations at  $\delta_{\text{H}} 3.72$  (q,  $J 6.5$  Hz), which was reported for the floridanine at  $\delta_{\text{H}} 3.03$  m. The positions of the signals of H-13 at  $\delta_{\text{H}} 1.47$  m, and of H<sub>2</sub>-14 at  $\delta_{\text{H}} 1.69$  (d,  $J 14.0$  Hz) and  $\delta_{\text{H}} 1.53$  (dd,  $J 14.0$ ,  $10.0$  Hz) were also different from the reported for these same protons (H-13 at  $\delta_{\text{H}} 1.89$  m and H<sub>2</sub>-14 at  $\delta_{\text{H}} 2.35$  m) in the floridanine. These discrepancies could be due to different positions of the acetoxy group in **5** and in the floridanine.<sup>9</sup> In order to clarify these structural differences, an X-ray diffraction experiment (Figure 2) was performed establishing that compound **5** had indeed the structure reported for the floridanine.

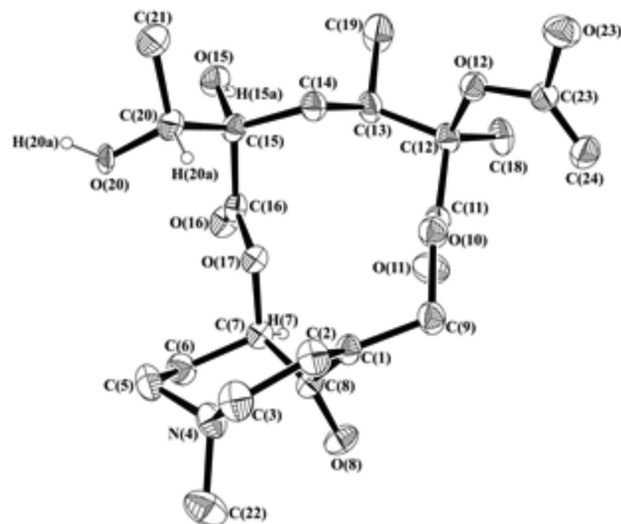


Figure 2. ORTEP representation of **5**.

Consequently, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data (obtained by means of 2D NMR spectroscopy) should correct those from the literature.<sup>9</sup> The absolute stereochemistry of the floridanine (**5**) (*7R*, *12R*, *13R*, *15S* and *20R*) was determined by the anomalous dispersion method with  $\text{Cu K}_\alpha$  radiation, used in the X-ray experiment, which afforded an absolute structure parameter of 0.08 (4).

## Conclusions

The presence of pyrrolidizine alkaloids is in agreement with the chemistry of many genera of the tribe Senecioneae, but the absence of sesquiterpenes as well as the presence of acyclic diterpenes establish a clear chemotaxonomic difference between *Villasenoria* and its related genera *Telanthophora*, *Senecio* and *Pittocaulon* and support its position in a new genus.

## Experimental

### General experimental procedures

Melting points were determined on a Fisher-Jones melting point apparatus and are uncorrected. Optical rotations were determined on a Perkin-Elmer 343 polarimeter. Circular dichroism was obtained on a Jasco J-720 spectropolarimeter. UV and IR spectra were recorded on a spectrophotometer Shimadzu UV 16U and a Bruker Tensor 27 spectrometer, respectively. 1D and 2D NMR spectra were obtained on a Bruker Avance III 400 MHz or on a Varian-Unity Inova 500 MHz spectrometer with tetramethylsilane (TMS) as internal standard. Electron ionization mass spectrometry (EIMS) analyses were determined on a Bruker Daltonics Analysis 3.2 mass spectrometer. HRESIMS analyses were performed on a Bruker MicrOTOF II mass spectrometer with a mass resolution of 16.500 FWHM (full width at half maximum), mass interval 50-20.000  $m/z$  and speed of 40 Hz. Fast atom bombardment mass spectrometry (FABMS) analyses were obtained on a JEOL JMS-SX102A mass spectrometer operated with an acceleration voltage of 10 kV, and the samples were desorbed from a nitrobenzyl alcohol matrix using 6 kV xenon atoms. HRFABMS analyses were performed at a 10,000 resolution using electric field scans and polyethylene glycol ions (Fluka 200 and 300) as the reference material. Column chromatography was carried out under vacuum on silica gel G-60 (Merck, Darmstadt, Germany). Analytical thin layer chromatography (TLC) was carried out on silica gel 60-G  $F_{254}$  or RP-18W/UV<sub>254</sub> (Macherey-Nagel, Germany) and preparative TLC on silica gel G-200  $F_{254}$ , layer thickness of 2.0 mm, or RP-18W/UV<sub>254</sub>, layer thickness of 1.0 mm.

### Plant material

*Villasenoria orcuttii* (Greenm.) B. L. Clark was collected in San Miguel Soyaltepec, Tuxtepec, Oaxaca, México, in January 2009. A voucher specimen was deposited at the Herbarium del Instituto de Biología, UNAM, México (MEXU 1256447).

### Extraction and isolation

Dried and ground aerial parts (276 g) and roots (116 g) of *V. orcuttii* were separately and successively extracted with hexane and methanol. Solvents were removed under reduced pressure to obtain the respective extracts. The methanolic extracts were partitioned with EtOAc- $\text{H}_2\text{O}$ . The aqueous extracts, which gave positive test with the Dragendorff alkaloid reagent, were treated with  $\text{Zn/aq.H}_2\text{SO}_4$ <sup>14</sup> to give the alkaloidal residues. The hexanic extract of roots (820 mg) was fractionated by vacuum column chromatography (VCC) using hexane-EtOAc mixtures in increasing gradient of polarity. Fractions eluted with hexane-EtOAc 19:1 (65 mg) were purified by flash column chromatography (FCC) (hexane-acetone 19:1) to obtain compound **2** (25 mg). Fractions eluted with hexane-EtOAc 9:1 afforded phytane-1,2,3-triol<sup>4,5</sup> (**1**, colorless oil, 361 mg). The hexanic extract of aerial parts (2.9 g) was submitted to VCC using hexane-acetone mixtures as gradient elution system to afford fractions A-C eluted with hexane-acetone 49:1, 19:1 and 9:1 mixtures, respectively. Fraction A (268 mg) was purified by FCC eluted with  $\text{CH}_2\text{Cl}_2$  to obtain a mixture of  $\beta$ -sitosterol-stigmasterol (38 mg). Fractions B (150 mg) produced by FCC eluted with hexane-acetone 19:1 compound **2** (24 mg). Fraction C (550 mg) by two successive FCC eluted with hexane-acetone 9:1 and  $\text{CH}_2\text{Cl}_2$ , respectively, afforded 250 mg of compound **1**. The ethyl acetate extract of the aerial parts (3.0 g) was purified by VCC eluting with hexane-EtOAc mixtures in gradient of increasing polarity to afford compound **1** (15 mg) from the hexane-EtOAc 9:1 mixtures, and from fractions eluted with hexane-EtOAc 4:1, a mixture (45 mg) which by preparative TLC (hexane-acetone 4:1) produced methyl ferulate<sup>10</sup> (**6**, white needles, mp 66-67 °C, 10 mg). The ethyl acetate extract of roots (1.5 g) purified by the same way as extract of aerial parts afforded 20 mg of **1**, from the hexane-EtOAc 9:1 mixtures, and from fractions eluted with hexane-EtOAc 7:3, a mixture (95 mg) which was purified by RPTLC (reversed-phase TLC) (MeOH- $\text{H}_2\text{O}$  3:2  $\times$  4) followed of FCC (hexane-acetone 7:3) to produce compound **3** (25 mg). The alkaloidal extract of roots (480 mg) was purified by VCC ( $\text{CH}_2\text{Cl}_2$ -MeOH in increasing gradient of polarity) to

afford, from CH<sub>2</sub>Cl<sub>2</sub>-MeOH 98:2 mixtures, pterolactame<sup>11</sup> (**7**, colorless needles, mp 55-56 °C, 32 mg) and tyramine<sup>12</sup> (**8**, white crystals, mp 160-162 °C, 98 mg), fraction E from CH<sub>2</sub>Cl<sub>2</sub>-MeOH 95:5, and fraction F from CH<sub>2</sub>Cl<sub>2</sub>-MeOH 9:1 eluates. Fraction E (65 mg) was submitted to FCC (CH<sub>2</sub>Cl<sub>2</sub>-MeOH 95:5) followed by a preparative TLC (CH<sub>2</sub>Cl<sub>2</sub>-MeOH-NH<sub>4</sub>OH 95:4.9:0.1 × 2) to afford florosenine<sup>6-8</sup> (**4**, mp 99-101 °C, [α]<sub>D</sub><sup>25</sup> + 30.5, *c* 0.2, CHCl<sub>3</sub>, 5 mg). Fraction F (102 mg) afforded after two successive FCC (CH<sub>2</sub>Cl<sub>2</sub>-MeOH 9:1) and a preparative TLC (CH<sub>2</sub>Cl<sub>2</sub>-MeOH-NH<sub>4</sub>OH 95:4.9:0.1 × 3) floridanine (**5**, 12 mg).<sup>6,9</sup> The alkaloidal extract of aerial parts (450 mg) was worked up as described for the root alkaloidal extract to afford **4** (3.5 mg), **5** (10 mg), **7** (17 mg) and **8** (35 mg).

#### Selective acetylation of phytane-1,2,3-triol (**1**)

Compound **1** (0.28 mmol), acetylchloride (0.28 mmol) and *i*Pr<sub>2</sub>EtN (0.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) were stirred at -70 °C for 3 h and then 1 h at room temperature.<sup>13</sup> The reaction mixture was washed with HCl (5%) and NaHCO<sub>3</sub> to obtain 87 mg of a mixture which was purified by FCC (hexane-acetone 85:15) to obtain 35 mg (34 %) of compound **2**.

#### Compound **2**

Colorless oil; [α]<sub>D</sub><sup>25</sup> + 5.0 (*c* 0.11, CHCl<sub>3</sub>); IR (CHCl<sub>3</sub>)  $\nu_{\max}$ /cm<sup>-1</sup> 3455, 1742; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.32 (dd, 1H, *J* 11.6, 2.8 Hz, H1a), 4.09 (dd, 1H, *J* 11.6, 8.4 Hz, H1b), 3.69 (dd, 1H, *J* 8.4, 2.8 Hz, H2), 1.06-1.32 (m, 21H, H4 to H15), 2.12 (s, 3H, CH<sub>3</sub>CO), 1.23 (s, 3H, H17), 0.84-0.88 (m, 12H, H16, H18, H19, H20); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.4 (CH<sub>3</sub>CO), 75.7 (C2), 73.6 (C3), 65.9 (C1), 39.4, 37.7, 37.6, 37.4, 37.3, 37.2, 24.8, 24.5, 20.7 (C4 to C6, C8 to C10, C12 to C14), 32.8, 32.7, 27.7 (C15, C11, C7), 23.5 (C17), 22.7, 22.6, 19.7, 18.6 (C16 and C18 to C20), 20.9 (CH<sub>3</sub>CO); HRESIMS *m/z* 395.3146 [M + Na]<sup>+</sup> (C<sub>22</sub>H<sub>44</sub>NaO<sub>4</sub> requires 395.3132).

#### Compound **3**

Colorless oil; [α]<sub>D</sub><sup>25</sup> + 11.0 (*c* 0.21, CHCl<sub>3</sub>); IR (CHCl<sub>3</sub>)  $\nu_{\max}$ /cm<sup>-1</sup> 3433, 1603, 1460; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.93 (br quint, 1H, *J* 1.0 Hz, H16a), 4.84 (br quint, 1H, *J* 1.5 Hz, H16b), 4.03 (br dd, 1H, *J* 11.0, 6.0 Hz, H14), 3.78 (d, 2H, *J* 5.0 Hz, H1), 3.49 (br t, 1H, *J* 5.0 Hz, H2), 1.72 (s, 3H, H20), 1.23 (s, 3H, H17), 1.05-1.60 (m, 18H, H4 to H13), 0.86\* (d, 3H, *J* 6.5 Hz, H18), 0.87\* (d, 3H, *J* 6.5 Hz, H19), \*interchangeable signals; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 147.5 (C15), 111.2 (C16), 76.5 (C14), 76.1 (C2), 74.7 (C3), 63.9 (C1), 38.4, 37.5, 37.2, 37.1, 32.3, 24.3, 24.2, 20.9 (C4 to C6, C8 to C10, C12, C13), 32.7, 32.5 (C11, C7), 23.7 (C17), 20.9 (C18 and C19) 17.5

(C20); HRESIMS *m/z* 367.2832 [M + Na]<sup>+</sup> (C<sub>20</sub>H<sub>40</sub>NaO<sub>4</sub> requires 367.2819).

#### Floridanine (**5**)

Colorless prism from hexane-EtOAc, mp 199-200 °C; [α]<sub>D</sub><sup>25</sup> + 68.0 (*c* 0.10, CHCl<sub>3</sub>); IR (CHCl<sub>3</sub>)  $\nu_{\max}$ /cm<sup>-1</sup> 3691, 3518, 1735, 1602; CD (*c* 4.5 × 10<sup>-5</sup> mol L<sup>-1</sup>, EtOH) Δε<sub>209 nm</sub> + 18.6; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.09 (br t, 1H, *J* 2.0 Hz, H2), 5.15 (d, 1H, *J* 11.0 Hz, H9a), 4.98 (t, 1H, *J* 2.5 Hz, H7), 4.44 (br d, 1H, *J* 11.0 Hz, H9b), 3.72 (q, 1H, *J* 6.5 Hz, H20), 3.46 (br d, 1H, *J* 17.5 Hz, H3a), 3.32 (br d, 1H, *J* 17.5 Hz, H3b), 2.90 (m, 1H, H5a), 2.85 (m, 1H, H5b), 2.60 (dddd, 1H, *J* 14.0, 12.0, 7.5, 2.5 Hz, H6a), 2.31 (br t, 1H, *J* 14.0 Hz, H6b), 2.08 (s, 6H, H22, CH<sub>3</sub>CO), 1.69 (d, 1H, *J* 14.0 Hz, H14a), 1.64 (s, 3H, H18), 1.53 (dd, 1H, *J* 14.0, 10.0 Hz, H14b), 1.47 (m, 1H, H13), 1.24 (d, 3H, *J* 6.5 Hz, H21), 1.19 (d, 3H, *J* 6.5 Hz, H19); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 186.9 (C8), 174.6 (C16), 171.2 (C11), 169.9 (CH<sub>3</sub>CO), 136.8 (C2), 133.9 (C1), 83.9 (C12), 81.9 (C15), 79.1 (C7), 72.7 (C20), 64.2 (C9), 59.5 (C3), 53.7 (C5), 40.3 (C22), 39.7 (C13), 36.3 (C6), 35.8 (C14), 21.6 (C18), 21.4 (CH<sub>3</sub>CO), 17.1 (C21), 14.6 (C19); EIMS *m/z* 441 [M]<sup>+</sup> (30), 397 [C<sub>20</sub>H<sub>31</sub>NO<sub>7</sub>]<sup>+</sup> (30), 354 [C<sub>18</sub>H<sub>28</sub>NO<sub>6</sub>]<sup>+</sup> (90), 168 [C<sub>9</sub>H<sub>14</sub>NO<sub>2</sub>]<sup>+</sup> (100), 149 [C<sub>9</sub>H<sub>11</sub>NO]<sup>+</sup> (65), 122 [C<sub>7</sub>H<sub>8</sub>NO]<sup>+</sup> (50), 110 [C<sub>6</sub>H<sub>8</sub>NO]<sup>+</sup> (48); HRFABMS *m/z* 442.2080 [M + H]<sup>+</sup> (C<sub>21</sub>H<sub>32</sub>NO<sub>9</sub> requires 442.2077).

#### Crystal data of **5**

C<sub>21</sub>H<sub>31</sub>NO<sub>9</sub>·0.8 (CH<sub>2</sub>Cl<sub>2</sub>), MW = 509.43, *T* = 100(2) K, λ = 1.54178 Å, orthorhombic, space group P2(1)2(1)2(1). Unit cell dimensions *a* = 8.6486(2) Å, *b* = 12.2669(2) Å, *c* = 24.8567(5) Å, α = 90°, β = 90°, γ = 90°, *V* = 2637.08(9) Å<sup>3</sup>, *Z* = 4, density (calculated) = 1.283 Mg m<sup>-3</sup>, absorption coefficient = 2.257 mm<sup>-1</sup>, *F*(000) = 1078, crystal size: 0.29 × 0.18 × 0.16 mm<sup>3</sup>, theta range for data collection: 4.02 to 66.74°, index ranges: -10 ≤ *h* ≤ 10, -14 ≤ *k* ≤ 14, -29 ≤ *l* ≤ 29, reflections collected: 37883, independent reflections: 4661 [R(int) = 0.0217], completeness to theta = 66.74° 99.6%, absorption correction = semi-empirical from equivalents, max. and min. transmission = 0.7141 and 0.5636, refinement method = full-matrix least-squares on *F*<sup>2</sup>, data / restraints / parameters 4661 / 664 / 532, goodness-of-fit on *F*<sup>2</sup> = 1.057, final *R* indices [I > 2σ(I)], *R*<sub>1</sub> = 0.0495, *wR*<sub>2</sub> = 0.1466, *R* indices (all data), *R*<sub>1</sub> = 0.0505, *wR*<sub>2</sub> = 0.1486; absolute structure parameter = 0.08(4); largest diffraction peak and hole = 0.569 and -0.195 e Å<sup>-3</sup>, respectively; single crystals of **5** were mounted at 100 K on nylon loops and the data were collected on a Bruker APEX DUO diffractometer equipped with an Apex II CCD detector using Incoatec IμS with multilayer optic, Cu K<sub>α</sub> radiation. Frames were

collected by omega scans and integrated using SAINT software package. Semi-empirical absorption correction (SADABS) was applied. The structure was solved by direct methods (SHELXS programs), and refined by the full-matrix least-squares on  $F^2$  with SHELXL-97<sup>15</sup> using the SHELXLE GUI.<sup>16</sup> All non-hydrogen atoms were refined anisotropically. The disordered was refined using the following geometry and  $U_{ij}$  restraints and constraints implemented in the SHELXL-97 program: SIMU, DELU, SAME and DFIX. Crystallographic data for the structure of **5** were deposited in the Cambridge Crystallographic Data Center (deposition No. CCDC 930369).

### Supplementary Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **1** and **4**, <sup>1</sup>H and <sup>13</sup>C NMR and 2D NMR experiments of compounds **2**, **3** and **5**, HRESIMS of compounds **2** and **3**, and crystal refinement data of **5** are available free of charge at <http://jbcbs.bq.org.br> as PDF file.

### Acknowledgements

We are indebted to Beatriz Quiróz, Ma. de los Angeles Peña, Elizabeth Huerta, Isabel Chávez, Héctor Ríos, Rubén Gaviño, Rocío Patiño, Javier Pérez, Luis Velasco, Carmen Márquez and Lizbeth Triana for technical assistance.

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Submitted: February 19, 2013

Published online: June 21, 2013