

## New Rearranged Limonoids from *Harrisonia perforata*

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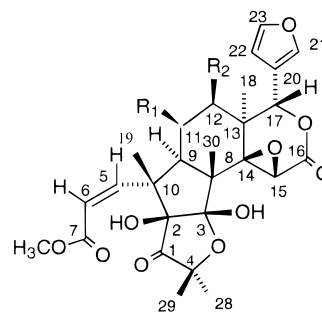
Two new rearranged limonoids, named haperforine A (**1**) and haperforine E (**2**), were isolated from a sample of *Harrisonia perforata* leaves collected in Center Vietnam and their structures determined by X-ray diffraction analysis. The structure of a minor compound was established as 12-desacetylhaperforine A (**3**) by chemical correlation. Their NMR and mass spectroscopic properties are reported.

*Harrisonia perforata* (Blanco) Merr. (Simaroubaceae) is a bush common throughout all Southeast Asia (Vietnam, Philippines, China). In Vietnamese folk medicine, it is used to treat itching,<sup>1</sup> and in neighboring countries it is also used as a remedy for diarrhea and dysentery.<sup>2,3</sup> Chemical investigations have shown the presence of limonoids, with perforatin,<sup>4,5</sup> perforatinolone,<sup>6</sup> and perforine A,<sup>7</sup> tetranor-triterpenes in the obacunol series<sup>8</sup> isolated from the leaves. Quassinoids were also identified from the root bark of this plant.<sup>7</sup> Other species, such as *Harrisonia abyssinica*<sup>9,10</sup> and *Harrisonia brownii*,<sup>11</sup> also provided limonoids of this type. In this paper we report the isolation and structure elucidation of three new limonoids that we isolated from the leaves of *H. perforata* collected in the Daklak district, in Center Vietnam.

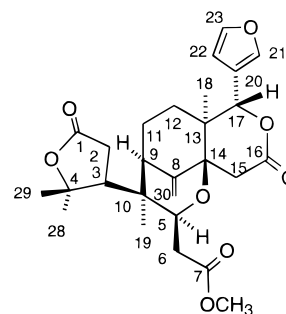
Limonoids were isolated from ground, dried leaves of *H. perforata* according to the procedure described by J. Polonsky for the isolation of the bitter principles of the Simaroubaceae, with slight modifications.<sup>13</sup> The crude extract was separated by successive column and thin layer chromatographies with various eluting systems and yielded two major pure compounds, haperforine A (**1**) and haperforine E (**2**). A minor, more polar compound structurally related to **1**, 12-desacetylhaperforine A (**3**), was also isolated by preparative TLC. The new compounds were characterized by complex rearranged skeletons.<sup>12</sup>

<sup>1</sup>H NMR analysis of **1** (C<sub>31</sub>H<sub>36</sub>O<sub>14</sub>) indicated the presence of a 3-substituted furan residue ( $\delta$  6.3, 7.3, and 7.4 as singlets for H-22, H-23, and H-21, respectively) and showed peaks for three methine carbons [C-CH-CH(OAc)-CH(OAc)-C] and two acetyl methyls, a methyl singlet, and an AB system for two olefinic protons (C-HC=CH-CO<sub>2</sub>CH<sub>3</sub>). The NOESY experiment showed that this olefinic bond was *Z*. Two exchangeable tertiary alcohols were characterized ( $\delta_{\text{H}}$  3.82 and 5.25) and five carbonyls ( $\delta$  167.2, 170.1, 170.5, 167.4, and 204.2) were identified. The extra oxygen was attributed to a trisubstituted epoxide, as indicated by a proton singlet at  $\delta$  4.3. These data are very similar to those described for harrisonin (**4**) and 12 $\beta$ -acetoxyharrisonin (**5**), limonoids isolated from *H. abyssinica* Oliv.<sup>9,10</sup> and of which the revised structures have been published recently.<sup>10</sup> Thus, **1** is 11 $\beta$ ,12 $\beta$ -acetoxyharrisonin. This conclusion was confirmed by X-ray crystallographic

analysis, which established the structure and relative stereochemistry (Figure 1).<sup>14</sup> The molecule is shown with the absolute configuration found for the limonoids previously isolated from this plant.<sup>3,5</sup>



- 1** R<sub>1</sub>=R<sub>2</sub>=OAc Haperforine A  
**3** R<sub>1</sub>=OAc R<sub>2</sub>=OH 12-desacetylhaperforine A  
**4** R<sub>1</sub>=R<sub>2</sub>=H  
**5** R<sub>1</sub>=H R<sub>2</sub>=OAc



**2**  
Haperforine E

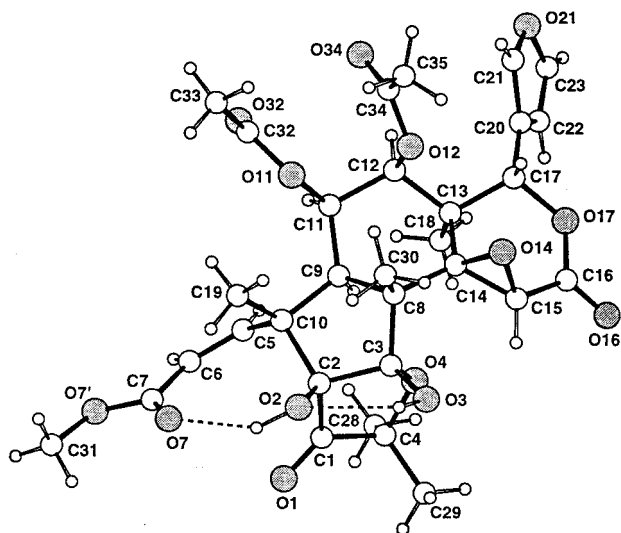
The molecule is arc shaped, showing many oxygen atoms. The propenoyl chain at C-10 is axial, on the  $\alpha$  face of the molecule, and is firmly held to the rest of the molecule by means of intramolecular hydrogen bonds involving the hydroxyl group (OH-2) with O-7 [distances O-2...O-7 = 2.963(3) Å, H-O-2...O-7 = 2.10(3) Å, angle O-H...O = 143°] and the oxygen atom O-2 with the hydroxyl group OH-3 [O-3...O-2 = 2.702(3) Å, H-O-3...O-2 = 2.18 Å, angle O-H...O = 110.3°]. Moreover, the hydrogen atom of hydroxyl group OH-3 is also engaged in a strong intermolecular hydrogen bond with O-16 of the nearest neighboring molecule [located at  $-0.5 + x, 1.5 + y, 1 - z$  with O-3...O-16 = 2.924(3) Å, H-O-3...O-16 = 2.10(3) Å, angle O-H...O =

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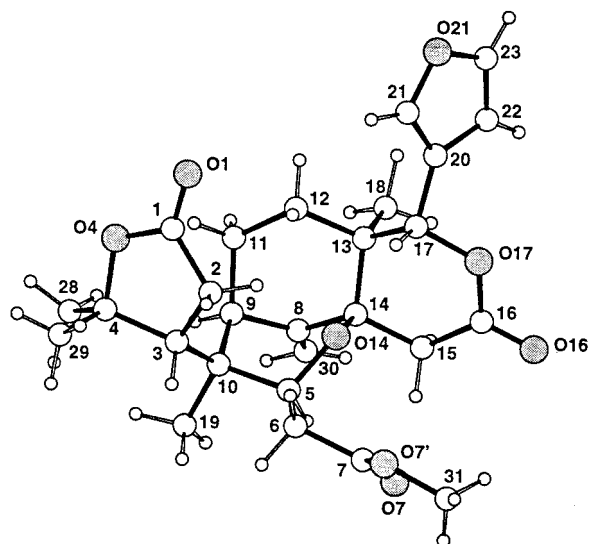
**Figure 1.** Crystal structure of **1**.

143°]. The two five-membered rings are cis-fused (dihedral angle of 70.7°) and adopt an envelope conformation with atoms C-3 and C-8 as the flaps, respectively distant at 0.483 (2) and 0.661 (3) Å from the respective mean plane formed by the other four atoms. The six-membered ring **C** (C-8 to C-14) exhibits a twist-boat conformation with atoms C-9 and C-13 situated at, respectively, -0.550 (3) and -0.620 (3) Å from the distorted plane of the other four atoms (C-8, C-11, C-12, and C-14). Ring **D** (C-13 to C-17) adopts the 1,3 diplanar conformation of cyclohexene, a flattened half-chair with atoms C-13 and C-17 at a distance of -0.487 (3) and 0.38 (3) Å, respectively, from the mean plane (C-14, C-15, C-16, and O-17). The furan ring is nearly perpendicular to ring **D** (torsion angle C-13-C-17-C-20-C-21 = 99.6°).

From a more polar fraction, a minor compound, having only one acetoxy group, was identified as 12-desacetyl-haperforine A (**3**), this was shown by the presence at  $\delta$  3.98 of H-12, coupling with a free OH ( $J = 4$ ) in its  $^1\text{H}$  NMR spectrum. Acetylation of **1** afforded **3**.

Haperforine E (**2**) ( $\text{C}_{25}\text{H}_{35}\text{O}_8$ ) was isolated by crystallization (MeOH) from fractions eluted by toluene/ether in the first chromatography of the crude extract.  $^1\text{H}$  NMR analysis of **2** showed signals at  $\delta$  0.88, 1.06, 1.52, and 1.64 for methyl groups; at 4.90 and 5.18 for an exomethylene; at 3.62 (dd) and 2.46 (ABX) for  $\text{OCH}-\text{CH}_2-\text{C}=\text{O}$ , and at 6.38, 7.38, and 7.45 for an unconjugated 3-monosubstituted furan ring. Signals characteristic of  $\text{CH}-\text{CH}_2-\text{CH}_2$ ,  $\text{CH}-\text{CH}_2$ ,  $\text{C}-\text{CH}_2-\text{C}=\text{O}$  groups were also present. Three carbonyl groups, represented by a carbomethoxy group, a  $\gamma$  lactone and a  $\delta$  lactone at  $\delta$  171.3, 175.4, and 169.8, respectively, in  $^{13}\text{C}$  NMR, were identified.

X-ray crystallographic analysis established the structure and relative stereochemistry as **2**.<sup>14</sup> The crystal structure is shown in Figure 2, with the absolute configuration of limonoids previously isolated from the same plant.<sup>3,5</sup> The molecule is formed of three six-membered rings to which were fixed a dimethylated lactone and a furan ring at C-10 and C-17, respectively. Ring **C** (C-8, C-9, C-11 to C-14) appears as a flattened chair, with atoms C-8 and C-12 deviating by -0.763 (3) and 0.529 (3) Å, respectively, from the mean plane formed by the other four atoms. The second ring **D** (C-13, C-14, C-15 to C-17) adopts an envelope conformation with C-13 at a distance of -0.684 (3) Å from the mean plane. The third ring exhibits a twist-boat conformation with atoms C-9 and O-14 at a distance of



**Figure 2.** Crystal structure of **2**.

0.572(3) and 0.528(1) Å, respectively, from the distorted mean plane formed by C-5, C-8, C-10, and C-14. With respect to this ring system, the furan and the lactone are tilted, as shown, by torsion angles: C-13-C-17-C-20-C-21 of 91.4(2)° and C-9-C-10-C-3-C-2 of -71.1(2)°.

### Experimental Section

**General Experimental Procedures.** Melting points were determined in capillary tubes and are uncorrected. Optical rotations,  $[\alpha]_D$ , were measured in  $\text{CHCl}_3$  with 0.5% EtOH, at room temperature, on a Perkin-Elmer 241 polarimeter. IR spectra were determined with a Nicolet FT-IR 205 spectrometer and UV spectra with a Perkin-Elmer Lambda 205 spectrometer.  $^1\text{H}$  NMR spectra were obtained in  $\text{CDCl}_3$ , unless otherwise stated. Chemical shifts ( $\delta$ ) are expressed in parts per million (ppm), coupling constants are in hertz (Hz) and are registered with Bruker WP-300 and WP-400 instruments.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WP-300 instrument. Mass spectra were run on AEI MS-50 or AEI MS-9 spectrographs. Column chromatography was performed on Merck Kieselgel 60, flash column chromatography on Merck Kieselgel 60H. Analytical TLC was performed using Si gel precoated foils, visualized by spraying with 1% anisaldehyde reagent and 50% aqueous  $\text{H}_2\text{SO}_4$  and heating.

**Plant Material.** The *H. perforata* plant material was identified by the Museum of the Botanical Garden of Ho-Chi-Minh-ville, where a voucher specimen has been deposited.

**Extraction and Isolation of Limonoids.** The 25% aqueous EtOH extract from dried leaves (1000 g and 2.5 L of EtOH) was treated with lead acetate (400 mL of a 30% aqueous solution) and filtered. Addition of a  $\text{Na}_2\text{SO}_4$  solution to the filtrate gave a precipitate of lead sulfate, which was separated by filtration. Limonoids were adsorbed on active charcoal (30 g), which was filtered, dried at 50 °C for 24 h, and extracted with  $\text{CHCl}_3$  in a Soxhlet apparatus. Evaporation of the solvent gave a residue (2.42 g, 0.25%) of crude limonoids.

**Haperforine A (1).** A dry crude extract (17.5 g) prepared as described above (from 7 kg of dried leaves) was dissolved in toluene (40 mL) and chromatographed over a Si gel 60H column (100 g) and eluted with toluene/ether 1:1. Each 100-mL fraction was evaporated to dryness, and the residue was weighed and analyzed by TLC. The first fractions (400 mL) gave a residue (7.48 g) that afforded, by crystallization (MeOH), pure **1** (130 mg), mp 238–240° (MeOH),  $[\alpha]_D = +51.8^\circ$  ( $\text{CHCl}_3$ ,  $c$  1.05); UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 209 nm (4.32); IR (Nujol)  $\nu_{\text{max}}$  3468 (OH), 1743 (C=O), 1712 (C=O), 1243 (C-O), 1200 (C-O), 1050 (C-O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.18 (3H, s,  $\text{CH}_3$ -29), 1.28 (3H, s,  $\text{CH}_3$ -18), 1.40 (6H, s,  $\text{CH}_3$ -28,  $\text{CH}_3$ -30), 1.58 (3H, s,  $\text{CH}_3$ -19), 2.0 (3H, s,  $\text{COCH}_3$ , acetoxy-

11), 2.50 (3H, s, COCH<sub>3</sub>, acetoxy-12), 3.0 (1H, d, *J* = 4, H-9), 3.80 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.82 (1H, br s, OH), 4.30 (1H, s, H-15), 5.16 (1H, d, *J* = 4, H-12), 5.25 (1H, br s, OH), 5.80 (1H, AB, *J* = 12, H-6), 6.08 (1H, AB, *J* = 12, H-5), 5.86 (1H, t, *J* = 4, H-11), 6.0 (1H, s, H-17), 6.30 (1H, t, *J* = 1, H-22), 7.30 (1H, d, *J* = 1, H-23), 7.40 (1H, t, *J* = 1, H-21); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 16.1 (CH<sub>3</sub>-18), 16.5 (CH<sub>3</sub>-30), 19.4 (CH<sub>3</sub>-19), 21.4 (COCH<sub>3</sub>, acetoxy-12), 21.6 (COCH<sub>3</sub>, acetoxy-11), 24.5 (CH<sub>3</sub>-29), 27.9 (CH<sub>3</sub>-28), 42.8 (C-13), 48.5 (CH-9), 49.8 (C-8), 51.1 (C-10), 52.7 (OCH<sub>3</sub>), 55.0 (CH-15), 63.9 (CH-11), 66.6 (C-14), 71.8 (CH-12), 75.9 (CH-17), 81.7 (C-4), 87.8 (C-2), 108.5 (C-3), 109.9 (CH-22), 120.1 (C-20), 123.9 (CH-6), 142.1 (CH-23), 144.2 (CH-21), 152.2 (CH-5), 167.2 (C-7), 167.5 (C-16), 170.1 (C=O, acetyl-11), 170.5 (C=O, acetyl-12), 204.17 (C-1); 2D HETCOR, NOESY, and HMBC NMR experiments (CDCl<sub>3</sub>, 400 MHz) led to these assignments; HRCIMS *m/z* 33.2180 (calcd for C<sub>31</sub>H<sub>37</sub>O<sub>14</sub> 633.2183); *anal.* C 58.84%, H 5.74%, O 35.42% calcd for C<sub>31</sub>H<sub>36</sub>O<sub>14</sub>, C 58.86%, H 5.74%, O 35.42%.

**Crystal Data:** colorless crystal (0.13 × 0.40 × 0.53 mm) grown from MeOH, C<sub>31</sub>H<sub>36</sub>O<sub>14</sub>, *M<sub>w</sub>* = 632.62, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *Z* = 4, *a* = 11.374(6), *b* = 11.608(6), *c* = 24.267(12) Å, *V* = 3204(3) Å<sup>3</sup>, *d<sub>c</sub>* = 1.31 g cm<sup>-3</sup>, *F*(000) = 1336, λ(Cu Kα) = 1.5418 Å, μ = 0.84 mm<sup>-1</sup>; 4275 measured intensities (−9 ≤ *h* ≤ 13, *k*: 0 → 13, *l*: 0 → 28), 4053 unique (*R<sub>int</sub>* = 0.040) of which 3790 observed with *I* ≥ 2.0 σ(*I*).

**Data Collection and Structure Refinement.** Intensity data were measured on a Nonius CAD-4 diffractometer using graphite monochromated Cu Kα radiation and the (θ−2θ) scan technique up to θ = 66°. Cell parameters were refined from 25 well-centered reflections with 13.5° ≤ θ ≤ 23.2°. The structure was solved by direct methods using SHELXS86<sup>15</sup> and refined by full-matrix least-squares based upon unique *F*<sup>2</sup> with SHELXL93.<sup>16</sup> All the hydrogen atoms were located in difference maps and fitted at theoretical positions, except for those of the hydroxyl groups. They were assigned an isotropic displacement parameter equivalent to that of the bonded carbon atom plus 20% (30% for the methyl groups). Thus, refinement of 414 variables converged to *R*<sub>1</sub>(*F*) = 0.0454 (for the 3790 observed reflections) and *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.1227 (for all the 4047 data with goodness-of-fit *S* = 1.089). The residual electron density was found between −0.24 and 0.27 e Å<sup>-3</sup>. In the crystal packing, intermolecular hydrogen bonds of 2.924(3) Å were observed between the hydroxyl groups OH-3 and the oxygen atoms O-16 of the nearest molecules.

**Haperforine E (2).** After isolation of **1**, the following combined fractions (700 mL) were evaporated and by crystallization (MeOH) gave **2** (120 mg), mp 225–226° (EtOH), [α]<sub>D</sub> = −52° (CHCl<sub>3</sub>, *c* 1); IR (film) ν<sub>max</sub> 1767 and 1744 (C=O), 1658 (C=C), 1507 and 3136 (furan), 1405, 1250, 1039 (C–O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 0.88 (3H, s, CH<sub>3</sub>-18), 1.06 (3H, s, CH<sub>3</sub>-19), 1.18 (1H, m, H-12α), 1.52 (3H, s, CH<sub>3</sub>-29), 1.64 (3H, s, CH<sub>3</sub>-28), 1.85 (2H, m, CH<sub>2</sub>-12β, CH<sub>2</sub>-11α), 2.06 (1H, m, CH<sub>2</sub>-11β), 2.26 (1H, dd, *J* = 6, *J*' = 11, H-3), 2.36 and 2.42 (2H, ABX, *J* = 16, *J*' = 3, *J*' = 11, CH<sub>2</sub>-6), 2.52 (1H, d, *J* = 4, H-9), 2.78 and 2.87 (2H, AB, *J* = 18, CH<sub>2</sub>-15), 2.88 (1H, ABX, *J* = 11, *J*' = 18, H-2β), 3.32 (1H, ABX, *J* = 6.5, *J*' = 18, H-2α), 3.62 (1H, dd, *J* = 3, *J*' = 11, H-5), 3.70 ((3H, s, OCH<sub>3</sub>), 4.90 (1H, s, H-30a), 5.18 (1H, s, H-30b), 5.62 (1H, s, H-17), 6.38 (1H, t, *J* = 1, H-22), 7.38 (1H, d, *J* = 1, H-23), 7.45 (1H, t, *J* = 1, H-21); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 14.5 (CH<sub>3</sub>-18), 24.8 (CH<sub>3</sub>-28), 26.3 (CH<sub>2</sub>-11), 26.7 (CH<sub>3</sub>-19), 30.1 (CH<sub>2</sub>-12), 32.6 (CH<sub>2</sub>-15), 33.2 (CH<sub>3</sub>-29), 33.7 (CH<sub>2</sub>-2), 35.1 (CH<sub>2</sub>-6), 41.5 (C-13), 48.0 (C-10), 48.8 (CH-9), 50.8 (CH-3), 52.3 (OCH<sub>3</sub>), 78.4 (CH-5), 79.6 (CH-17), 81.9 (C-14), 87.6 (C-4), 109.8 (CH-22), 111.7 (CH<sub>2</sub>-30), 120.8 (C-20), 140.6 (CH-23), 142.9 (CH-21), 146.5 (C-8), 169.8 (C-16), 171.3 (C-7), 175.4 (C-1). 2D HETCOR, NOESY, and HMBC NMR (CDCl<sub>3</sub>, 400 MHz) experiments led to these assignments; HRCIMS *m/z* 487.2343 (calcd for C<sub>27</sub>H<sub>35</sub>O<sub>8</sub> 487.2331); *anal.* C 66.18%, H 7.01%, O 26.82%, calcd for C<sub>27</sub>H<sub>34</sub>O<sub>8</sub>, C 66.65%, H 7.005%, O 26.32%.

**Crystal data:** colorless crystal (0.03 × 0.20 × 0.46 mm) grown from MeOH; C<sub>27</sub>H<sub>34</sub>O<sub>8</sub>, *M<sub>w</sub>* = 486.56, monoclinic, space group *P*2<sub>1</sub>, *Z* = 2, *a* = 8.340(7), *b* = 14.799(5), *c* = 10.036(8) Å, *b* = 93.46(2)°, *V* = 1236(1) Å<sup>3</sup>, *d<sub>c</sub>* = 1.31 g cm<sup>-3</sup>, *F*(000) = 520,

λ(Cu Kα) = 1.5418 Å, μ = 0.75 mm<sup>-1</sup>; 3250 measured intensities, 3053 unique of which 2911 observed with *I* > 2.0 σ(*I*).

**Data Collection and Structure Refinement.** Intensity data were measured on a Nonius CAD-4 diffractometer using graphite monochromated Cu Kα radiation and the (q − 2q) scan technique up to θ = 66°. The structure was solved by direct methods using SHELXS86<sup>15</sup> and refined by large block-matrix least-squares with SHELXL93.<sup>16</sup> The hydrogen atoms, all located in difference Fourier maps, were fitted at theoretical positions and assigned an isotropic thermal factor equivalent to that of the bonded carbon atom plus 20%. Convergence was reached at *R*<sub>1</sub>(*F*) = 0.041 (for 2911 observed reflections) and *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.127 (for all 3053 data, goodness of fit = 1.086). The residual electron density was found between −0.23 and 0.20 e Å<sup>-3</sup>. In the crystal packing, only normal van der Waals contacts were observed.

**12-Desacetylhaperforine (3).** A dry crude extract (3.24 g) dissolved in toluene was chromatographed on Si gel (150 g). Elution with toluene/ether 1:1 yielded a residue (308 mg) that was purified on preparative TLC leading to **3** (150 mg), mp 185° (MeOH), [α]<sub>D</sub> = +49° (CHCl<sub>3</sub>, *c* 0.9); IR (film) ν<sub>max</sub> 3440 (OH), 1729 (C=O), 1622 (C=C), 1436, 1390, 1271 (C–O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 1.16 (3H, s, CH<sub>3</sub>-29), 1.18 (3H, s, CH<sub>3</sub>-18), 1.38 (3H, s, CH<sub>3</sub>-30), 1.40 (3H, s, CH<sub>3</sub>-28), 1.65 (3H, s, CH<sub>3</sub>-19), 2.18 (3H, s, COCH<sub>3</sub>), 2.64 (1H, d, *J* = 4, OH), 2.98 (1H, d, *J* = 7, H-9), 3.80 (3H, s, OCH<sub>3</sub>), 3.82 (1H, s, OH), 3.98 (1H, dd, *J* = 7, *J*' = 4, H-12α), 4.24 (1H, s, H-15), 5.12 (1H, br s, OH), 5.40 (1H, t, *J* = 7, H-11), 5.80 (1H, AB, *J* = 12, H-6), 6.08 (1H, AB, *J* = 12, H-5), 6.28 (1H, s, H-17), 6.45 (1H, s, H-22), 7.40 (1H, s, H-23), 7.50 (1H, s, H-21); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 16.1 (CH<sub>3</sub>-18) 16.8 (CH<sub>3</sub>-30) 19.8 (CH<sub>3</sub>-19), 22.1 (COCH<sub>3</sub>), 24.5 (CH<sub>3</sub>-29), 28.0 (CH<sub>3</sub>-28), 43.6 (C-13), 49.0 (CH-9), 49.6 (C-8), 51.1 (C-10), 52.7 (OCH<sub>3</sub>), 54.8 (CH-15), 65.9 (C-14), 67.5 (CH-11), 70.4 (CH-12), 76.5 (CH-17), 81.7 (C-4), 88.1 (C-2), 108.5 (C-3), 110.5 (CH-22), 120.8 (C-20), 124.0 (CH-6), 142.0 (CH-23), 143.8 (CH-21), 152.5 (CH-5), 167.2 (C-7), 168.2 (C-16), 170.8 (C=O, acetyl), 205 (C-1). 2D NMR HETCOR and HMBC (CDCl<sub>3</sub>, 400 MHz) experiments led to these assignments; HRCIMS *m/z* 591.2119 (calcd for C<sub>29</sub>H<sub>35</sub>O<sub>13</sub> 591.2077), 573.2006 (calcd for C<sub>29</sub>H<sub>33</sub>O<sub>12</sub> 573.1972), 555.1848 (calcd for C<sub>29</sub>H<sub>31</sub>O<sub>11</sub> 555.1866).

**Acetylation of 12-Desacetylhaperforine A.** A solution of **3** (22 mg) in acetic anhydride (0.5 mL) and pyridine (0.5 mL) was reacted at room temperature for 24 h. Addition of an aqueous solution of NaHCO<sub>3</sub> (5 mL) was followed by extraction with ether (3 × 5 mL). The organic phase was dried over MgSO<sub>4</sub> and evaporated to give a residue that was purified by preparative TLC (ether as eluent) to afford a compound (5 mg) whose physical properties (<sup>1</sup>H NMR, MS, TLC) were identical to those of **1**.

**Supporting Information Available:** Crystallographic data are available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

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Copies of the data can be obtained, free of charge, on application to the Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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