

densed into a dry ice-acetone-cooled (jacketed) addition funnel at  $-78^{\circ}\text{C}$ . The chlorine was added dropwise to 250 mL of dry methylene chloride at  $-78^{\circ}\text{C}$ . To the resultant pale yellow solution, under a static nitrogen pressure, was added 11.0 g (92 mmol) of 2-(methylthio)-*N*-methylacetamide<sup>6</sup> in 10 mL of dry methylene chloride. A white precipitate formed. After the reaction mixture had been stirred for 20 min, a solution of 23.44 g (176 mmol) of 1,2,3,4-tetrahydroquinoline (1) in 25 mL of dry methylene chloride was added dropwise. The reaction mixture was stirred for 3 h at  $-70^{\circ}\text{C}$ , followed by addition of 40 mL of triethylamine. After being stirred for an additional hour at  $-70^{\circ}\text{C}$ , the reaction mixture was allowed to warm to ambient temperature (overnight). The organic mixture was washed with aqueous sodium carbonate solution, dried over anhydrous sodium carbonate, filtered, and concentrated to give a solid. This solid was recrystallized from ether-hexane to give 15.7 g (62.8 mmol, 71%) of white crystalline product: mp  $137\text{--}139^{\circ}\text{C}$ ; IR (CDCl<sub>3</sub>) 3380 (w), 2940 (w), 2850 (vw), 1670 (s), 1610 (w), 1520 (m), 1450 (w), 1410 (w), 1380 (vw), 1310 (m), 1190 (w), 1115 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.11-2.13 (m, 2 H), 2.03 (s, 3 H), 2.57-2.92 (m, 5 H), 3.16-3.48 (m, 2 H), 4.47 (s, 1 H), 5.03 (br s, 1 H), 6.36-7.10 (complex m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.27 (q), 21.40 (t), 26.44 (q), 27.44 (t), 41.95 (t), 53.16 (d), 116.18 (d), 119.75 (s), 122.69 (s), 125.89 (d), 129.14 (d), 143.02 (s), 170.66 (s); exact mass, *m/e* 250.1143 (calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>OS, *m/e* 250.1139).

Anal. Calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>OS: C, 62.37; H, 7.25; N, 11.19. Found: C, 62.43; H, 7.27; N, 11.16.

**2-(1,2,3,4-Tetrahydroquinolin-8-yl)-*N*-methylacetamide (5).**

To 7.5 g (30 mmol) of  $\alpha$ -(methylthio)- $\alpha$ -(1,2,3,4-tetrahydroquinolin-8-yl)-*N*-methylacetamide (4) in a mixture of 100 mL of acetone and 100 mL of denatured ethanol was added 10 level teaspoons (approximately 30 g) of activated Raney nickel, and the reaction mixture was stirred for 30 min. The reaction mixture was filtered through a fritted glass funnel. The spent catalyst was washed with 50 mL of acetone. The combined filtrates were concentrated in vacuo. The resulting residue was taken up in 100 mL of methylene chloride and dried over anhydrous magnesium sulfate. Filtration and concentration gave 5.8 g (28.2 mmol, 94%) of product. Distillation gave 5.2 g (25.5 mmol, 85%) of pure 5: bp  $175\text{--}190^{\circ}\text{C}$  (0.2 mm); IR (CDCl<sub>3</sub>) 3420 (w), 3310 (vw), 2930 (w), 2850 (w), 1670 (s), 1610 (w), 1530 (m), 1415 (w), 1310 (w), 1280 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.69-2.12 (m, 2 H), 2.58-2.90 (m, 5 H), 3.34 (s, 2 H), 3.18-3.47 (m, 2 H), 4.78 (br s, 1 H), 6.09 (br s, 1 H), 6.35-7.06 (complex m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.47 (t), 26.11 (q), 27.2 (t), 40.30 (t), 41.83 (t), 116.13 (d), 118.85 (s), 122.01 (s), 128.26 (d), 128.61 (d), 143.39 (s), 171.91 (s); exact mass, *m/e* 204.1260 (calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O, *m/e* 204.1262).

Anal. Calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.58; H, 7.87; N, 13.58.

**2-Methyl-1,2,9,10-tetrahydro-8*H*-pyrido[3,2,1-*jk*][1,3]-benzodiazepin-3(4*H*)-one (6).** To 2.04 g (10 mmol) of 2-(1,2,3,4-tetrahydroquinolin-8-yl)-*N*-methylacetamide (5) in 25 mL of benzene was added 0.30 g (10 mmol) of paraformaldehyde, and the reaction mixture was refluxed overnight. The reaction mixture was concentrated to give a syrup, which was distilled to give 2.01 g (9.3 mmol, 93%) [bp  $155\text{--}170^{\circ}\text{C}$  (0.2 mm)] of a syrup that gradually crystallized. Recrystallization from ether-hexane gave 1.65 g (7.6 mmol, 76%) of 6 as crystals: mp  $92.0\text{--}93.5^{\circ}\text{C}$ ; IR (CDCl<sub>3</sub>) 2950 (w), 1670 (s), 1600 (w), 1480 (m), 1460 (m), 1400 (w), 1370 (w), 1330 (w), 1270 (w), 1210 (w), 1180 (w), 1110 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.78 (quintet, 2 H), 2.63 (t, 2 H), 3.06 (s, 3 H), 3.78 (t, 2 H), 3.93 (s, 2 H), 4.73 (s, 2 H), 6.40-6.98 (complex m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  23.28 (t), 27.27 (t), 34.37 (q), 43.29 (t), 50.35 (t), 67.41 (t), 117.79 (s), 118.59 (d), 127.19 (s), 127.42 (d), 130.00 (d), 143.04 (s), 171.94 (s); exact mass, *m/e* 216.1265 (calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O, *m/e* 216.1261).

Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.18; H, 7.49; N, 12.93.

**8-[2-(Methylamino)ethyl]-1,2,3,4-tetrahydroquinoline (7).**  $\alpha$ -(Methylthio)- $\alpha$ -(1,2,3,4-tetrahydroquinolin-8-yl)-*N*-methylacetamide (4) (7.5 g, 30 mmol) was desulfurized with activated Raney nickel as described for the preparation of 5 (vide supra). The resulting undistilled product was dissolved in 200 mL of dry tetrahydrofuran, and 2.0 g (52.7 mmol) of lithium aluminum hydride was added. The reaction mixture was refluxed for 4 h and hydrolyzed by adding, in sequence (slowly), 2 mL of water,

2 mL of 15% sodium hydroxide solution, and 6 mL of water. The resulting mixture was filtered through a fritted glass funnel, and the filtrate was concentrated to give an oil. Distillation of the oil gave 4.07 g (21.4 mmol, 71%) of 7: bp  $106\text{--}112^{\circ}\text{C}$  (0.2 mm); IR (neat) 3300 (w), 2920 (m), 2830 (m), 1595 (m), 1500 (m), 1450 (m), 1350 (w), 1315 (m), 1280 (m), 1190 (w), 1115 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.70-2.17 (m, 2 H), 2.38 (s, 3 H), 2.54-2.98 (m, 6 H), 3.16-3.44 (m, 2 H), 6.33-7.02 (complex m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.86 (t), 27.36 (t), 31.62 (t), 36.37 (q), 41.01 (t), 51.34 (t), 116.17 (d), 121.28 (s), 123.5 (s), 127.41 (d), 127.64 (d), 142.80 (s); exact mass, *m/e* 190.1476 (calcd for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>, *m/e* 190.1470).

Anal. Calcd for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.45; H, 9.54; N, 14.60.

**1,2,3,4,9,10-Hexahydro-2-methyl-8*H*-pyrido[3,2,1-*jk*][1,3]-benzodiazepine (8).** To 0.95 g (5 mmol) of 8-[2-(methylamino)ethyl]-1,2,3,4-tetrahydroquinoline (7) in 20 mL of benzene was added 0.15 g (5 mmol) of paraformaldehyde, and the reaction mixture was refluxed overnight. Concentration of the reaction mixture gave an oil, which was distilled to give 0.92 g (4.55 mmol, 91%) of 8: bp  $100\text{--}102^{\circ}\text{C}$  (0.2 mm); IR (neat) 2960 (m), 2840 (w), 1605 (w), 1500 (m), 1370 (w), 1320 (m), 1300 (m), 1260 (w), 1220 (w), 1200 (w), 1120 (m), 1080 (w), 1060 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.56-2.05 (m, 2 H), 2.47 (s, 3 H), 2.58-3.00 (m, 6 H), 3.12-3.43 (m, 2 H), 3.90 (s, 2 H), 6.49-7.02 (complex m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.29 (t), 27.84 (t), 32.59 (t), 39.60 (q), 53.03 (t, 2 C), 77.86 (t), 119.35 (d), 126.03 (s), 126.89 (d), 128.13 (d), 131.80 (s), 147.72 (s); exact mass, *m/e* 202.1471 (calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>, *m/e* 202.1470).

Anal. Calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.10; H, 9.03; N, 13.99.

**2-Methyl-3,4,9,10-tetrahydro-8*H*-pyrido[3,2,1-*jk*][1,3]-benzodiazepin-1(2*H*)-one (9).** To 0.95 g (5 mmol) of 8-[2-(methylamino)ethyl]-1,2,3,4-tetrahydroquinoline (7) in 50 mL of dry tetrahydrofuran was added 0.81 g (5 mmol) of 1,1'-carbonyldiimidazole, and the reaction mixture was refluxed for 1 h. To this reaction mixture was added 2.25 g (20 mmol) of potassium *tert*-butoxide, and the reaction mixture was refluxed for 2 h. The reaction mixture was concentrated, and 100 mL of methylene chloride was added. The mixture was washed with water, dried over anhydrous sodium carbonate, filtered, and concentrated to give a solid. This solid was recrystallized from ether-hexane to give 0.61 g (2.8 mmol, 56%) of 9: mp  $121\text{--}123^{\circ}\text{C}$ ; IR (CDCl<sub>3</sub>) 2940 (w), 1620 (ms), 1490 (m), 1440 (m), 1400 (w), 1350 (w), 1330 (w), 1310 (w), 1250 (w), 1180 (w), 1060 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.72-2.13 (m, 2 H), 2.76 (s, 3 H), 2.63-3.12 (m, 4 H), 3.20-3.85 (m, 4 H), 6.99 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  22.53 (t), 26.67 (t), 30.34 (t), 38.31 (q), 44.51 (t), 56.61 (t), 123.81 (d), 124.95 (d), 127.70 (d), 129.46 (s), 133.57 (s), 140.76 (s), 158.44 (s); exact mass, *m/e* 216.1260 (calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O, *m/e* 216.1261).

Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.16; H, 7.54; N, 12.93.

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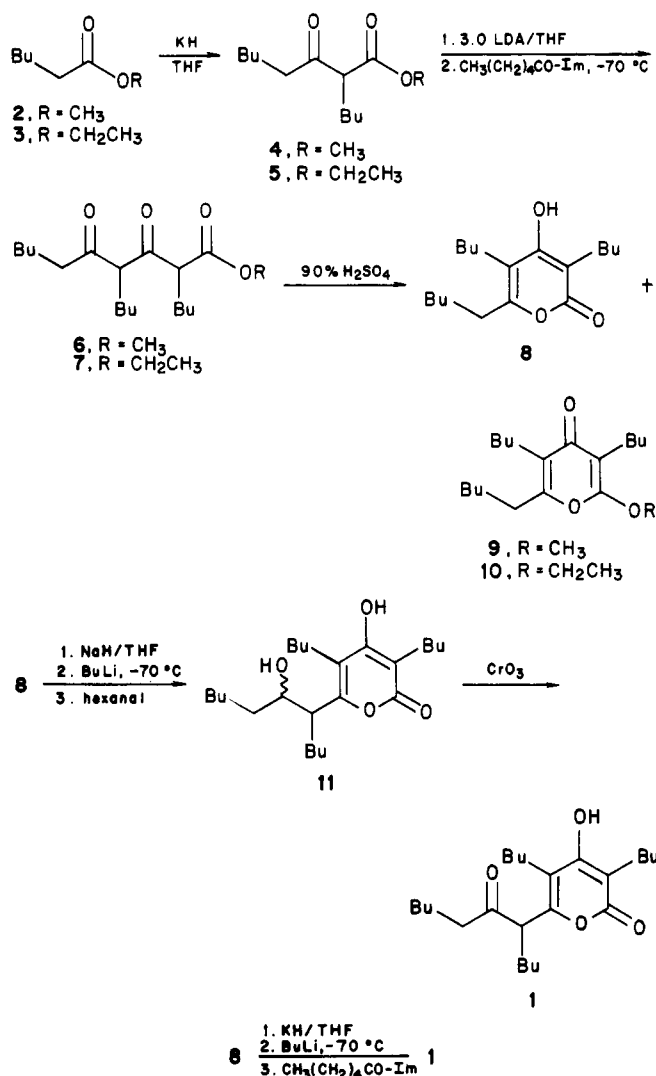
### A Short Synthesis of Elasinin

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Elasinin (1) is a complex trisubstituted 4-hydroxy-2-pyrene that has been isolated from culture broths of *Streptomyces norboritoensis*.<sup>1a,b</sup> It is a specific inhibitor

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of human leukocyte elastase, an important enzyme in the pathology of inflammatory diseases such as pulmonary emphysema.<sup>2</sup> Accounts of the structure determination of elasnin and its biosynthesis from polyketide intermediates have appeared.<sup>1c,d</sup> Preliminary reports of its synthesis have also been published.<sup>3,4</sup> We describe a short, practical synthesis of elasnin that allows facile preparation of this important 2-pyrone.

An analysis of the structure of elasnin reveals that it can be constructed by successive addition of three hexanoyl units to a hexanoate residue and lactonization to furnish the pyrone ring. Consequently we reasoned that a successful synthesis of elasnin could be achieved in three steps by first, hexanoylation of the appropriate  $\beta$ -keto ester 4; second, lactonization of the resultant diketo ester 6 to 2-pyrone 8; and third, hexanoylation of the 2-pyrone 8 dianion (Scheme I).

Toward this end, application of the Brown potassium hydride driven Claisen condensation<sup>5</sup> gave 2-butyl-3-oxoester 4 in excellent yield.  $\beta$ -Keto ester<sup>6</sup> 4

was converted to its lithium dienolate and acylated with *N*-hexanoylimidazole<sup>7</sup> to furnish methyl 2,4-dibutyl-3,5-dioxodecanoate (6) (60%). The usefulness of acyl imidazoles as acylating agents has been noted by others.<sup>8</sup> Cyclization of crude diketo ester 6 with 90% sulfuric acid followed by flash column chromatography of the mixture of  $\alpha$ - and  $\gamma$ -pyrones, 8 and 9, produced 3,5-dibutyl-6-pentyl-4-hydroxy-2-pyrone (8) in 79% yield. Initially, we used ethyl esters 3, 5, and 7 to obtain the intermediate 2-pyrone 8. However, cyclization of the  $\beta$ ,  $\gamma$ -diketo methyl ester 6 gave a significantly better yield of 8. For example, sulfuric acid lactonization of methyl ester 6 produces a 4.3:1 ratio of 2-pyrone to 4-pyrone (8/9), whereas ethyl ester 7 gives a 1.9:1 ratio of 8 to 10. This difference results in a 79% yield of 2-pyrone 8 from methyl ester 6, whereas ethyl ester 7 gives only a 53% yield of 8.

Dianions of 6-methyl-4-hydroxy-2-pyrone have been used frequently to elaborate position 7 through alkylation, acylation, and condensation reactions.<sup>9</sup> Pyrone 8 has a secondary carbon at the 6-position but, nonetheless, underwent successful dianion formation. Hexanoylation of the dianion of 8 with *N*-hexanoylimidazole gave elasnin (1) (17%), as a mixture with 8 after an initial chromatographic purification. Separation of 1 from 8 proved to be tedious and impractical. Elasnin was more readily prepared by condensing the dianion of 8 with *n*-hexanal to give dihydroelasnin (11) (25%), which was easily purified and isolated as a mixture of diastereomers. Treatment of 11 with Jones reagent gave racemic elasnin (1) (65%) as a colorless, viscous oil. The physical and spectroscopic properties of 1 were identical with those reported by Omura.<sup>1d</sup>

## Experimental Section

Melting points were determined on a Fischer-Johns melting point apparatus and are not corrected. Infrared spectra were taken on a Perkin-Elmer Model 283 or 681 spectrometer. Nuclear magnetic resonance (NMR) spectra were taken on a Varian Associates Model T-60, A-60A, or FT-80 NMR spectrometer. Chemical shifts are expressed in parts per million downfield from the internal standard tetramethylsilane ( $\delta = 0$ ). Mass spectra were recorded on a Kratos MS-30 mass spectrometer. Gas chromatography (GC) analyses were performed on Hewlett Packard Model 5700 and Varian 1400 gas chromatographs. Microanalysis were determined by the Searle Laboratories Microanalytical Department. All solvents used were reagent grade. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Thin-layer chromatography was carried out on plates coated with Merck silica gel G. Flash column<sup>10</sup> chromatographic separations were carried out by using silica gel (E. Merck silica gel 60, 230-400-mesh ASTM).

**Ethyl 2-Butyl-3-oxooctanoate (5).** Ethyl hexanoate, 11.1 g (77 mmol), was added dropwise to a stirred slurry of 3.4 g (85 mmol) of potassium hydride in 125 mL of dry tetrahydrofuran under argon at a rate that maintains the temperature below 35

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(3) The present work was reported in part at the Central and Great Lakes American Chemical Society Joint Regional Meeting, Dayton, OH, May 1981.

(4) Pfister, J. *Tetrahedron Lett.* 1980, 21, 1281.

(5) Brown, C. *Synthesis* 1975, 327.

°C. Vigorous hydrogen evolution occurs. After 1 h the reaction was quenched with 6 mL of acetic acid and 50 mL of water and 100 mL of diethyl ether was added. The ether layer was separated and the aqueous layer extracted twice with ether. The combined ether extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give 8.4 g (90%) of colorless oil, GC (6 ft, 1.2% Carbowax 20 M): 96% purity. Short path distillation at 82–92 °C (0.2 mm) gave 7.2 g (77%) of pure oil, GC (6 ft, 1.2% Carbowax 20 M); 99.9% purity: IR (CHCl<sub>3</sub>) 1745, 1720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88 (t, 6 H, CH<sub>3</sub>'s), 1.13 (t, 3 H, ester CH<sub>3</sub>), 1.08–2.08 (m, 12 H, envelope CH<sub>2</sub>'s), 2.50 (m, 2 H, CH<sub>2</sub>CO), 3.41 (t, 1 H, CH), 4.18 (q, 2 H, OCH<sub>2</sub>). Anal. Calcd for C<sub>14</sub>H<sub>26</sub>O<sub>3</sub>: C, 69.38; H, 10.81. Found: C, 69.45; H, 11.05.

**Methyl 2-butyl-3-oxooctanoate (4)** was prepared in the same manner as **5**. Short path distillation at 86–90 °C (0.4 mm) gave 13.9 g (67%), GC (6 ft, 1.2% Carbowax 20 M): 99% purity; IR (CHCl<sub>3</sub>) 1748, 1720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.89 (t, 6 H, CH<sub>3</sub>'s), 1.08–2.08 (m, 12 H, CH<sub>2</sub>'s), 2.52 (t, 2 H, CH<sub>2</sub>CO), 3.45 (t, 1 H, CH), 3.74 (s, 3 H, CH<sub>3</sub>O). Anal. Calcd for C<sub>13</sub>H<sub>24</sub>O<sub>3</sub>: C, 68.38; H, 10.59. Found: C, 68.78; H, 10.58.

**Methyl 2,4-Dibutyl-3,5-dioxodecanoate (6)**. To a solution of 40 mmol of lithium diisopropylamide (prepared from 8.4 mL of diisopropylamine and 16.1 mL of 2.48 M solution of *n*-butyllithium) in dry tetrahydrofuran (100 mL) at –10 °C under argon was added 4.57 g (20 mmol) of methyl 2-butyl-3-oxooctanoate (**4**) in tetrahydrofuran (30 mL). The solution was stirred for 1 h at 0 °C and cooled to –20 °C, and an additional 20 mmol of lithium diisopropylamide was prepared by adding 8.06 mL of 2.48 M *n*-butyllithium. The reaction was cooled to –78 °C and a solution of 3.22 g (20 mmol) of 1-(1-oxohexyl)-1*H*-imidazole in 50 mL of tetrahydrofuran was added dropwise, and then the solution was stirred for 1 h. After being warmed to –40 °C, the reaction was quenched with 10 mL of acetic acid and added to a mixture of 200 mL of ether and 100 mL of water. The ether layer was separated and the aqueous layer was extracted twice with 100 mL of ether. The combined ether extracts were washed with 2 N hydrochloric acid, saturated sodium bicarbonate solution, and brine, dried (anhydrous magnesium sulfate), filtered, and concentrated in vacuo to give 5.86 g of light yellow oil. GC (6 ft Carbowax 20 M) gave 60% of **6**, 30% of **4**, and 10% of an unknown component. The crude diketone ester was used for preparation of the 2-pyrone **8** without purification.

**3,5-Dibutyl-4-hydroxy-6-pentyl-2-pyrone (8)**. The crude methyl 2,5-dibutyl-3,5-dioxodecanoate (**6**), 4 g (7.35 mmol), was dissolved in 40 g of 90% sulfuric acid and left overnight at room temperature. The acid was poured into 1.5 L of water and the acidic solution was extracted 3 times with 250 mL of ether. The ether extracts were washed with saturated sodium bicarbonate and brine. After drying (anhydrous magnesium sulfate) and filtration, the ether was removed by evaporation to give 3.1 g of an orange oil. The oil was purified by flash column chromatography (1:9 ethyl acetate–hexane) to provide 0.41 g (18%) of 2-methoxy-3,5-dibutyl-6-pentyl-4-pyrone (**9**) as a clear oil [*R*<sub>f</sub> (2:5 ethyl acetate–hexane) 0.39; IR (CHCl<sub>3</sub>) 1670, 1590 cm<sup>-1</sup>; UV (MeOH) λ<sub>max</sub> 256 nm (ε 8915); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.90 (br t, 9

H, Me's), 1.38 (br m, 14 H, internal CH<sub>2</sub>'s), 2.43 (overlapping t's, 6 H, CH<sub>2</sub>'s on pyrone), 3.9 (s, 3 H, OCH<sub>3</sub>). Anal. Calcd for C<sub>19</sub>H<sub>32</sub>O<sub>3</sub>: C, 73.98; H, 10.46. Found: C, 73.89; H, 10.36.] and 1.7 g (79%) of crystalline 2-pyrone **8** [mp 66–67 °C; *R*<sub>f</sub> (2:5 ethyl acetate–hexane) 0.23; MS, *m/e* 294 (M<sup>+</sup>); IR (CHCl<sub>3</sub>) 3580, 1688 cm<sup>-1</sup>; UV (MeOH) λ<sub>max</sub> 293 nm (ε 8830); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.92 (br t, 9 H, CH<sub>3</sub>'s), 1.42 (br m, 14 H, internal CH<sub>2</sub>'s), 2.45 (br t, 6 H, CH<sub>2</sub>'s on pyrone). Anal. Calcd for C<sub>18</sub>H<sub>30</sub>O<sub>3</sub>: C, 73.43; H, 10.27. Found: C, 73.24; H, 10.59.]

**Dihydroelasnin (11)**. To a suspension of 188 mg (3.9 mmol) of sodium hydride in 25 mL of dry tetrahydrofuran under argon was added 1.05 g (3.5 mmol) of solid 2-pyrone **8**. The solution was stirred for 15 min after hydrogen evolution ceased. The solution was cooled to –78 °C, 1.7 mL of 2.54 M *n*-butyllithium (4.3 mmol) was added, and the solution was stirred for 1 h. The dianion solution was then warmed to –30 °C and stirred for 1 h, after which time 0.47 mL (392 mg, 3.91 mmol) of hexanal was added. The reaction was quenched with 5 mL of 1:9 acetic acid–water and added to 100 mL of ether, and the ether layer was separated. The ether was washed with water, saturated sodium bicarbonate solution, and brine and dried over anhydrous magnesium sulfate. Filtration and solvent evaporation gave 1.45 g of an oil that was purified by flash column chromatography (1:19 ethyl acetate–hexane) to give 355 mg (25%) of dihydroelasnin (**11**) as a glass that is a mixture of diastereomers: *R*<sub>f</sub> (1:4 ethyl acetate–hexane) 0.07 and 0.10; IR (CHCl<sub>3</sub>) 3570, 1690, 1575 cm<sup>-1</sup>; UV (MeOH) λ<sub>max</sub> 293 nm (ε 8155); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.87 (br t's, 12 H, CH<sub>3</sub>'s), 1.3 (br s, 22 H, internal CH<sub>2</sub>'s), 2.43 (br s, 4 H, CH<sub>2</sub>'s on pyrone), 2.73 (br s, 1 H, CH), 3.78 (br s, 1 H, CH). Anal. Calcd for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>: C, 73.05; H, 10.73. Found: C, 73.36; H, 10.85.

**Elasnin (1)**. Jones reagent, 1.5 mL (1.34 mmol), was added slowly to a solution of 340 mg (0.86 mmol) of dihydroelasnin (**11**) in 20 mL acetone at 0 °C. After being warmed to room temperature, the reaction was quenched with 1.0 mL of isopropyl alcohol, 100 mg of sodium bicarbonate was added, the solution was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in 50 mL of ether and the ether was washed with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to give 220 mg (65%) of elasnin (**1**) as a colorless, clear oil: *R*<sub>f</sub> (1:4 ethyl acetate–hexane) 0.30; IR (CCl<sub>4</sub>) 3580, 1715, 1665, 1635 cm<sup>-1</sup>; MS, *m/e* 392 (M<sup>+</sup>); UV (ethanol) λ<sub>max</sub> 291 nm (ε 7775); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.9 (t's, 12 H, CH<sub>3</sub>'s), 1.30 (br m, 2 H, internal CH<sub>2</sub>'s), 1.93 (br q, 2 H, CH<sub>2</sub>), 2.4 (t's, 4 H, CH<sub>2</sub>'s on pyrone), 3.59 (t, 1 H, CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.9, 14.1 (4 CH<sub>3</sub>'s), 22.5, 22.6, 22.8, 23.4, 24.6, 28.6, 29.8, 30.5, 31.5, 31.3, 32.0 (12 CH<sub>2</sub>'s), 40.3 (CH<sub>2</sub> adj to ketone), 54.8 (methine C), 104.6 (C-3), 115.5 (C-5), 155.0 (C-6), 165.3 (C-2), 207.3 (C-8). Anal. Calcd for C<sub>24</sub>H<sub>40</sub>O<sub>4</sub>: C, 73.43; H, 10.27. Found: C, 73.12; H, 10.52.

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