A solution of the 5'-protected triester (7, 0.230 g) in dichloromethane (25 mL) was cooled to 0 °C and was added to a stirred dichloromethane solution of trifluoroacetic acid (100 mL, 0.026 M) at 0 °C. After 25 min at 0 °C, the solution was treated with pyridine (2.7 mL) in dichloromethane (20 mL). The solution was evaporated, and the residue was dried under vacuum and dissolved in chloroform (1 mL) for application to the preparative TLC plates. The development of the plate and the isolation of the 5'-unprotected triester **8** (0.133 g, 70% yield) were carried out as described above.

The 5'-unprotected triester (**8**; 0.120 g) was mixed with pyridine (1.5 mL), water (1.5 mL), and triethylamine (0.14 mL) at 25 °C. The mixture was stirred for 36 h at 25 °C and was freeze-dried. The salt TpTp-DMG^{2-}[$(C_2H_5)_3NH^+$]$_2$ (**1a**; 0.057 g, 45% yield) was obtained in pure form by preparative TLC (two successive elutions by 2:1 chloroform/methanol in the same plate; extraction with the same solvent, 10 × 100 mL; precipitation as free-flowing powder from mininum of chloroform upon addition of acetone). The conversion of the triethylammonium salt **1a** into the calcium salt **1** was performed as follows. A solution of **1a** (0.116 g) in 2:1 chloroform/methanol (30 mL) was mixed with 3:48:47 chloroform/methanol/2 M aqueous calcium chloride (20 mL). The upper phase was discarded, and the procedure was repeated two additional times with the lower phase. The final lower phase was washed twice with 3:48:47 chloroform/methanol/water (20 mL) and evaporated. The residue was kept for 18 h (0.2 torr) to yield **1** (0.10 g).

Synthesis of DMG-pTpT (2; Cf Table I). A dichloromethane solution (1 mL) of 1,2-di-*O*-myristoyl-*sn*-glycerol (**6**; 0.256 g, 0.5 mmol) was added to a stirred dichloromethane solution (0.5 mL) of the pyrophosphate (**4**; 0.141 g, 0.5 mmol) containing triethylamine (0.07 mL) at 25 °C. After 2 h at 25 °C, the solution was evaporated to give the cyclic phosphate **9** (this compound is quite sensitive to moisture). A solution of the 5'-unprotected dinucleotide triester (**10**; 0.308 g, 0.5 mmol) in dimethylformamide (1 mL) was added to a solution containing the cyclic phosphate **9**, triethylamine (0.14 mL, ca. 1 mmol), and dichloromethane (2 mL) at 25 °C. After 36 h at 25 °C, the solution was evaporated, and the residue was dissolved in chloroform (1.5 mL) for application to preparative-TLC plates. The nucleotidophospholipid triester (**11**, 0.220 g, 35%) was isolated as described above (three successive elutions per plate utilizing 7:3:1 ethyl acetate/acetone/water, extraction with 2:1 chloroform/methanol, 5 × 50 mL).

The triester (**11**, 0.100 g) was mixed with pyridine (1.5 mL), water (1.5 mL), and triethylamine (0.14 mL). The mixture was stirred for 24 h at 25 °C and was freeze-dried. The salt, DMG-pTpT^{2-}[$(C_2H_5)_3NH^+$]$_2$ (**2a**, 0.050 g, 47%) was obtained in pure form by preparative TLC (two successive elutions per plate utilizing 2:1 chloroform/methanol as solvent; extraction with the same solvent, 10 × 100 mL; precipitation as free-flowing powder from chloroform upon addition of acetone). The conversion of the triethylammonium salt **2a** into the calcium salt **2** was performed as described above.

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Registry No. 1, 82732-09-0; **1a**, 82769-18-4; **2**, 82740-47-4; **2a**, 82795-53-7; **3**, 62930-01-2; **4**, 55894-94-5; **5**, 62930-09-0; **6**, 1069-82-5; **7**, 82732-10-3; **8**, 82732-11-4; **9**, 82263-08-9; **10**, 62962-23-6; **11**, 82740-48-5.

Synthesis of (±)-Lineatin, an Aggregation Pheromone of *Trypodendron lineatum*

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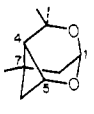
Abstract: A regioselective synthesis of lineatin (**1**) was accomplished, starting from anhydromevalonolactone (**8**). Photochemical cycloaddition of **8** with acetylene gave the cyclobutene **9**, which was converted to lactone **13** upon methylation followed by oxidation. Hydroboration–oxidation of **13** afforded a mixture of **14** and **15**, from which tosylate **18** was obtained. Reduction of **18** gave the endo hemiacetal **19**, which underwent an intramolecular displacement to produce **1**. Isolineatin (**2**) was obtained by reduction of **13** to hemiacetal **20**, followed by intramolecular oxymercuration with mercuric pivalate and reduction with sodium borohydride.

Lineatin (**1**), an aggregation pheromone from the frass of the female ambrosia beetle *Trypodendron lineatum* (Olivier),[1] has been shown to elicit powerful secondary attraction in laboratory[2] and field trials.[3] The extensive damage to fallen and sawn timber, especially Douglas fir, caused by *T. lineatum*[4] lends particular significance to this pheromone as a possible means for controlling this pest.[5] Originally formulated as either **1** or **2**,[1] lineatin was

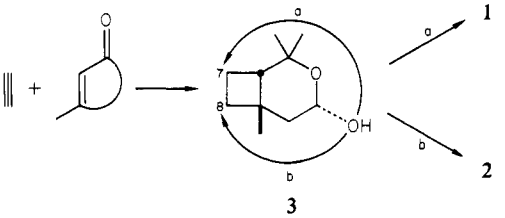


1

2

subsequently shown to be 3,3,7-trimethyl-2,9-dioxatricyclo-[3.3.1.0^{4,7}]nonane (**1**) by unambiguous synthesis.[6] Recently, a synthesis of (+)-**1** was described that established the absolute configuration of this biologically active enantiomer as 1*R*,4*S*,5*R*,7*R*.[7]

Scheme I



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The need for substantial quantities of lineatin for entomological work, coupled with the fact that previous preparations have yielded

(1) MacConnell, J. G.; Borden, J. H.; Silverstein, R. M.; Stokkink, E. *J. Chem. Ecol.* **1977**, *3*, 549.

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(3) Rudinsky, J. A.; Daterman, G. E. *Z. Angew. Entomol.* **1964**, *54*, 300. Rudinsky, J. A.; Daterman, G. E. *Can. Entomol.* **1964**, *96*, 1339. Chapman, J. A. *Ibid.* **1966**, *98*, 50.

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(5) Baker, R.; Evans, D. A. *Chem. Br.* **1980**, *16*, 412 and references cited.

(6) (a) Mori, K.; Sasaki, M. *Tetrahedron Lett.* **1979**, 1329. (b) Borden, J. H.; Hardley, J. R.; Johnston, B. D.; MacConnell, J. G.; Silverstein, R. M.; Slessor, K. N.; Swigar, A. A.; Wong, D. T. W. *J. Chem. Ecol.* **1979**, *5*, 681. (c) Mori, K.; Sasaki, M. *Tetrahedron* **1980**, *36*, 2197.

(7) Slessor, K. N.; Oehlschlager, A. C.; Johnston, B. D.; Pierce, H. D.; Grewel, S. K.; Wickremesinghe, L. K. G. *J. Org. Chem.* **1980**, *45*, 2290.

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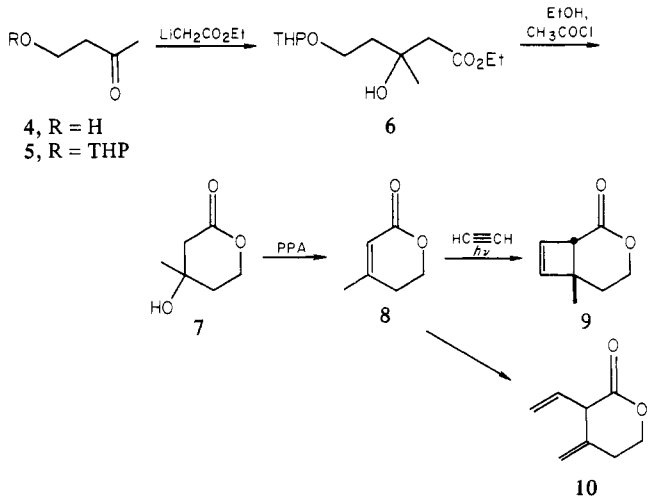
Scheme II

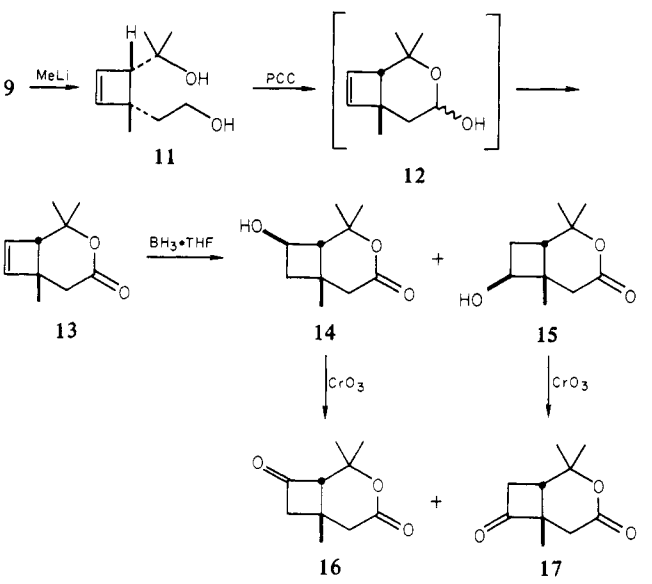


only meager amounts of the pheromone, prompted us to consider a new strategy for the synthesis of **1**. Our plan, outlined in Scheme I, takes advantage of a recent observation that photochemical [2 + 2] cycloaddition of acetylene to $\alpha\beta$-unsaturated carbonyl systems leads to cyclobutenes in good yield under certain conditions.[8] A suitably functionalized bicyclic hemiacetal, **3**, derived in this way, could provide access to **1** by intramolecular ether formation at C7 (path a) or to its isomer **2** by analogous cyclization at C8 (path b). The substitution pattern at the ring fusion of **3** appeared to offer several options for differentiation of paths a and b, and hence for regioselective synthesis of either **1** or **2**. Furthermore, the endo configuration of **3** required for closure to **1** and **2** was expected to be readily accessible via reduction of the corresponding δ-lactone from the convex (exo) face.

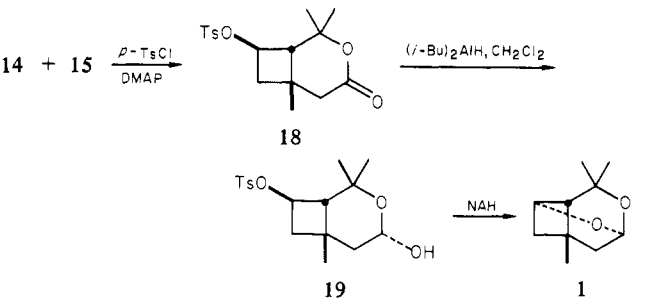
The substrate chosen for photochemical cycloaddition to acetylene was 5,6-dihydro-4-methyl-2-pyrone (anhydromevalonolactone, **8**). Although a satisfactory synthesis of this material has been described by Cornforth,[9] a more convenient preparation, particularly for large-scale work, was devised starting from 4-hydroxy-2-butanone (**4**) (see Scheme II). The latter was first converted to its tetrahydropyranyl ether **5**[10] and then treated with the lithium enolate of ethyl acetate.[11] The resulting β-hydroxy ester **6**, upon exposure to a trace of acetyl chloride in dry ethanol, suffered cleavage of the tetrahydropyranyl group and underwent spontaneous lactonization to give mevalonolactone **7** in 80% yield after distillation. In practice, it was more satisfactory to subject crude **7** to slow distillation over polyphosphoric acid;[9] this gave **8** directly in 89% yield from **6**.

Initial attempts to effect photochemical cycloaddition of acetylene to **8** in solvents such as ether and hexane were disappointing. Irradiation of the mixture through Pyrex or Corex glass with a 450-W Hanovia lamp gave little evidence of reaction, whereas illumination through Vycor produced large quantities of polymeric material. Interruption of the latter irradiation permitted isolation of the ene product **10**, which was itself photochemically reactive and may have been the source of the intractable material from this reaction. In any event, it was found that, when **8** in *acetonitrile* saturated with a stream of acetylene was irradiated through Vycor, smooth cycloaddition occurred to give **9** in 73% yield. This remarkable solvent effect renders the photochemical cycloaddition of acetylene an efficient and therefore valuable means for the preparation of 1,2-unsubstituted cyclobutenes and of cognate disubstituted cyclobutanes.[12] The selection of **8** as a photoaddend was predicated on the assumption that the lactone

Scheme III



Scheme IV



carbonyl of **9** would afford a suitable locus for siting the geminal methyl substituents of lineatin, and indeed, the reaction of **9** with methyllithium afforded the crystalline diol **11** in good yield (see Scheme III). Oxidation of **11** with pyridinium chlorochromate in methylene chloride led directly to the low-melting lactone **13**, presumably via hemiacetal **12**. The structure of **13**, obtained in 83% yield after chromatographic purification, was readily apparent from its IR spectrum, which showed the presence of a δ-lactone (1725 cm^{-1}), and from its ^1H NMR spectrum, which displayed two cyclobutene protons (δ 6.17) and three methyl singlets (δ 1.35, 1.38, and 1.43).

It was intended, at this stage, to employ the cyclobutene π bond for introducing functionality at C7. Unexpectedly, the double bond of **13** resisted hydroboration by disiamylborane and other hindered boranes, from which we had hoped to derive high regioselectivity,[13] and it was therefore necessary to resort to borane itself. After oxidation of the resulting alkylboranes with basic hydrogen peroxide, a mixture of two hydroxy lactones was obtained in 80% yield. Clean separation of these isomers was achieved by gas chromatography, which permitted their identification as **14** and **15** in the ratio 3:1, respectively. That these alcohols were regioisomers rather than stereoisomers was proven by the fact that they gave different cyclobutanones, **16** and **17**, upon oxidation. Moreover, comparison of the H7 and H8 signals in the NMR spectra of **14** and **15** left no doubt that the major alcohol was indeed the desired regioisomer **14**. In particular, the splitting pattern of H7 in **14** showed one cis (1 Hz) and two trans (7 Hz) couplings, thus indicating an exo configuration for the hydroxyl group in this isomer.[14] Lastly, a comparison of the NMR properties of **14** and its derived ketone **16** with data reported by Mori and Sasaki for the corresponding compounds prepared by

(8) White, J. D.; Matsui, T.; Thomas, J. A. *J. Org. Chem.* **1981**, *46*, 3376.
(9) Cornforth, J. W.; Cornforth, R. H.; Popjak, G.; Gore, I. *Biochem. J.* **1958**, 146.
(10) Coblentz, M.; Royer, J.; Dreux, J. *Bull. Soc. Chim. Fr.* **1963**, 1279.
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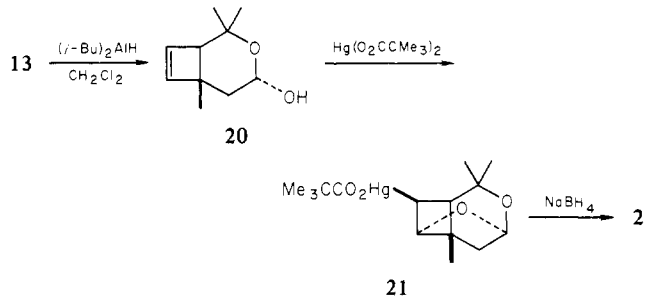
(13) Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975; pp 5–9.
(14) Eaton, P. E. *J. Am. Chem. Soc.* **1962**, *84*, 2344.

Scheme V



a different route[6c] revealed correspondence in all details. Although the configuration of **15** was not proven rigorously, it is likely that the hydroxyl group in this structure is also exo.

Fortunately, for the purpose of a lineatin synthesis, it proved unnecessary to separate **14** and **15**, since the less sterically hindered alcohol (**14**) underwent reaction with *p*-toluenesulfonyl chloride in pyridine containing a trace of 4-(dimethylamino)pyridine at a much faster rate than its isomer (see Scheme IV). The tosylate **18**, obtained in 66% yield after separation from unreacted **15**, was treated in dichloromethane at −78 °C with diisobutylaluminum hydride to give a single hemiacetal **19**, which, on the basis of a sterically controlled approach, is assigned the endo configuration shown. A Dreiding model of this epimer reveals that the hydroxyl group is ideally oriented for an intramolecular displacement of the exo tosylate, and when **19** was converted to its alkoxide with sodium hydride in ether, cyclization occurred spontaneously to give (±)-**1** in 67% yield. The IR, NMR, and mass spectra of our synthetic material exactly matched those of an authentic sample of lineatin supplied by Professor Oehlschlager.

Having demonstrated that path a of Scheme I affords a regioselective route to the racemic pheromone, we next considered alternatives for diverting **13** along path b to isolineatin (**2**). Intramolecular oxymercuration was selected for this purpose on the grounds that attack at the cyclobutene π bond of **13** by mercury(II) would result in placement of the electrophile at C7 for steric reasons,[15] and hence ether closure should take place at C8. Reduction of **13** in dichloromethane by diisobutylaluminum hydride at −78 °C afforded **20** in 95% yield (see Scheme V). This endo hemiacetal was treated with mercuric pivalate, a reagent which, in addition to its good solubility in THF, has been found to give higher regio- and stereoselectivity than conventional mercury(II) reagents in oxymercuration.[16] The intermediate alkylmercury complex **20** was reduced with sodium borohydride, and after purification by gas chromatography, isolineatin (**2**) was obtained in 42% yield. Spectral properties of **2** were in excellent agreement with those of an authentic sample of isolineatin.

Experimental Section

General Methods. All reactions were performed under an argon atmosphere unless otherwise specified, using standard syringe techniques for transfer of materials. Where necessary, organic solutions were dried over $MgSO_4$ and the product was isolated by filtration and evaporation of the filtrate on a Büchi rotary evaporator. Infrared (IR) spectra were measured on a Perkin-Elmer 727B spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained from a Varian EM-360A, HA-100, or FT-80A spectrometer. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as internal standard. Coupling constants (J) are given in hertz (Hz) with the following abbreviations for splitting patterns: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra (MS) were determined with a MAT CH-7 (electron impact) or a Finnigan 4023 (chemical ionization, CH_4) spectrometer. Exact mass measurements were made on a CEC-110B instrument by using the peak match technique. Elemental analyses were carried out by Micanal, Tucson, AZ. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Gas chromatography was carried out on a Varian Aerograph 2700 instrument with He carrier at 60 mL/min. Thin layer chromatography (TLC) was performed on Merck precoated silica plates (60F-254). Tetrahydrofuran (THF) was dried by distillation over sodium benzophenone ketyl. Dichloromethane was purified by washing with sulfuric acid and water, followed by distillation from phosphorus pentoxide.

Ethyl 3-Hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)pentanoate (6). To a solution of diisopropylamine (33 mL, 0.24 mol) in dry THF (200 mL) at 0 °C was added 1.6 M *n*-butyllithium (150 mL, 0.24 mol), and the mixture was stirred for 0.5 h. The solution was cooled to −78 °C, and ethyl acetate (21.1 g, 0.24 mol) was added, followed after 0.5 h by 4-(2-tetrahydropyranyloxy)butan-2-one (39.2 g, 0.23 mol). The mixture was stirred at −78 °C for 0.5 h and then quenched with 20% aqueous hydrochloric acid (60 mL). This mixture was added to water (500 mL) and extracted with ether (3 × 250 mL). The combined ethereal extract was washed with saturated aqueous sodium chloride, dried, and evaporated to give 46.2 g (80%) of **6** as a viscous sweet-smelling oil: IR (film) 3500, 1730, 1450, 1370, 1330, 1195, 1120, 1070, 1020, 970, 900, 860, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.64 (1 H, m) 4.20 (2 H, q, J = 7 Hz), 3.30–4.10 (4 H, m), 2.60 (2 H, s), 1.94 (2 H, t, J = 6 Hz), 1.64 (6 H, m), 1.34 (3 H, s), 1.30 (3 H, t, J = 7 Hz); MS, m/z 176, 158, 84.

4-Methyl-5,6-dihydro-2-pyrone (Anhydromevalonolactone, 8). To a solution of acetyl chloride (0.3 mL) in dry ethanol (300 mL) was added **6** (42.1 g, 0.16 mol), and the mixture was allowed to stand at room temperature for 10 h. The solvent and volatile byproducts were removed under vacuum (15 °C (0.3 torr)), leaving crude 3-hydroxy-3-methylvalerolactone (**7**). This material was distilled to give 16.6 g (80%) of **7**: bp 120–125 °C (0.3 torr); IR (film) 3450, 2950, 2920, 1720, 1475, 1400, 1275, 1240, 1130, 1080, 1020, 930, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (2 H, t, J = 7 Hz), 3.05 (1 H, s), 2.60 (2 H, s), 1.95 (2 H, t, J = 7 Hz), 1.40 (3 H, s). Addition of polyphosphoric acid (0.5 mL) to crude **7** obtained above, followed by slow distillation, afforded 18.1 g (89%) of **8** as a colorless oil: bp 65 °C (0.4 torr) (lit.[9] bp 118–120 °C (14 torr)); IR (film) 2940, 2925, 1700 cm^{-1}; NMR ($CDCl_3$) δ 5.84 (1 H, q, J = 1 Hz), 4.40 (2 H, t, J = 5 Hz), 2.44 (2 H, t, J = 7 Hz), 2.04 (3 H, S).

1-Methyl-4-oxabicyclo[4.2.0]oct-7-en-5-one (9). A solution of **8** (3.00 g, 0.027 mol) in dry acetonitrile (90 mL) saturated with a slow stream of acetylene was irradiated with a 450-W medium-pressure mercury lamp (Hanovia) through a Vycor Filter for 22 h. At this point, NMR indicated that 85–90% of **8** had been consumed. The mixture was evaporated and the residue was taken up into dichloromethane and chromatographed on Florisil. Elution with dichloromethane gave 2.60 g (73%) of **9** as a viscous oil: IR (film) 2950, 1795, 1450, 1375, 1290, 1250, 1220, 1170, 1110, 1090, 1050, 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23 (1 H, d, J = 3 Hz), 6.08 (1 H, d of d, J = 3, 1.5 Hz), 4.35 (2 H, t, J = 7 Hz), 3.24 (1 H, d, J = 1.5 Hz), 1.84 (2 H, t, J = 7 Hz), 1.33 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 24.2, 33.5, 47.0, 53.0, 65.7, 131.0, 145.1, 172.0; MS, m/z 138.068 (M^+), calcd for $C_8H_{10}O_2$ 138.068.

***cis*-3-(2-Hydroxyethyl)-4-(2-hydroxy-2-propyl)-3-methylcyclobutene (11).** To 1.5 M methyllithium (low halide) in ether (50 mL, 0.075 mol) at 0 °C was added slowly a solution of **9** (2.00 g, 0.015 mol) in 20 mL of ether. The mixture was stirred at 0 °C for 2 h and poured into ice-cold, saturated aqueous ammonium chloride. The mixture was extracted with ether (3 × 75 mL) and the ethereal extract was washed with brine (3 × 75 mL). The organic solution was dried and the solvent was evaporated to give a solid. This was crystallized from cyclohexane, affording 1.78 g (79%) of **11**: mp 55–57 °C; IR (film) 3400, 3010, 2970, 1635, 1450, 1370, 1220, 1160, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) 6.34 (1 H, d of d, J = 3, 1.5 Hz), 6.06 (1 H, d of d, J = 3, 1.5 Hz), 3.74 (2 H, t, J = 7 Hz), 2.50 (1 H, d, J = 1.5 Hz), 2.49 (s, OH), 1.92–2.33 (2 H, m), 1.71 (s, OH), 1.33 (3 H, s), 1.30 (3 H, s), 1.24 (3 H, s); MS, m/z 155 ($M^+ - CH_3$). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.51; H, 10.50.

***cis*-1,5,5-Trimethyl-4-oxabicyclo[4.2.0]oct-7-en-3-one (13).** To a suspension of pyridinium chlorochromate (1.95 g, 9.0 mmol) in dichloromethane (25 mL) was added a solution of **11** (1.00 g, 6.0 mmol) in dichloromethane (25 mL). The mixture was stirred for 1 h at room temperature, diluted with ether (100 mL), and passed through a short column of Florisil. The solvent was evaporated and the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (3:1) gave 0.82 g (83%) of **13** as an oil, which solidified on standing: mp 38–40 °C; IR (film) 3010, 2980, 1725, 1450, 1420, 1390, 1370, 1340, 1320, 1290, 1220, 1200, 1140, 1060, 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.25 (1 H, d, J = 3 Hz), 6.11 (1 H, d, J = 3 Hz), 2.65 (2 H, s), 2.60 (1 H, s), 1.43 (3 H, s), 1.38 (3 H, s), 1.35 (3 H, s); MS, m/z 166.099 (M^+, calcd for $C_{10}H_{14}O_2$ 166.099), 125, 109, 108, 91, 80, 79.

***exo*-7-Hydroxy-1,5,5-trimethyl-4-oxabicyclo[4.2.0]octan-3-one (14) and *exo*-8-Hydroxy-1,5,5-trimethyl-4-oxabicyclo[4.2.0]octan-3-one (15).** To a stirred solution of 1 M borane–THF (4 mL, 4 mmol) in dry THF (20 mL) at −10 °C was added dropwise a solution of **13** (0.50 g, 3.0 mmol) in dry THF (8 mL). The mixture was stirred at −10 °C for 3 h and quenched by careful addition of water. To the aqueous solution was added 3 M sodium hydroxide (10 mL), followed by 30% hydrogen per-

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(16) Sheldon, B. G. Ph.D. Dissertation, Oregon State University, 1981.

oxide (6 mL), and the mixture was stirred for 14 h at room temperature. This mixture was poured into brine containg 2% hydrochloric acid (100 mL) and extracted with ethyl acetate (4 × 40 mL). The organic extract was washed with brine, dried, and evaporated to leave a residue which was chromatographed on silica gel. Elution with hexane–ethyl acetate (1:1) gave 0.455 g (80%) of a mixture of **14** and **15**. Preparative gas chromatography of this mixture on a 0.25 in. × 4 ft column of 10% OV-17 on Chromosorb W at 200 °C cleanly separated **14** and **15** and showed that the ratio was 3:1, respectively. Alcohol **14**: retention 5.8 min; IR (film) 3380, 2950, 1720, 1450, 1420, 1390, 1290, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.17 (1 H, d of t, J = 7, 1 Hz), 2.43 (2 H, AB q, J = 16 Hz), 1.7–2.5 (3 H + OH, m), 1.40 (3 H, s), 1.37 (3 H, s), 1.30 (3 H, s); MS, m/z 184 (M^+), 169, 151, 141, 125, 123, 111, 109, 107. Alcohol **15**: retention 6.8 min; IR (film) 3400, 2950, 1720, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (1 H, br d, J = 8 Hz), 2.45 (2 H, s), 2.12 (1 H, m), 1.55 (2 H, br s), 1.37 (3 H, s), 1.28 (3 H, s), 1.23 (3 H, s); MS, m/z 169, 167, 151, 141, 125, 123, 111, 109, 107.

***cis*-1,5,5-Trimethyl-4-oxabicyclo[4.2.0]octan-3,7-dione (16) and *cis*-1,5,5-Trimethyl-4-oxabicyclo[4.2.0]octan-3,8-dione (17).** To an ice-cold solution of borane–THF (0.60 mL, 0.60 mmol) in dry THF (2 mL) was added dropwise a solution of **13** (0.100 g, 0.60 mmol) in THF (2 mL). The mixture was stirred for 1.5 h and carefully diluted with water. When gas evolution had ceased, a 0.7 M solution of Jones' reagent (4 mL) was added, and the mixture was stirred at room temperature for 5 h and poured into water. The aqueous solution was extracted with ether (3 × 20 mL), and the ethereal extract was washed with saturated aqueous sodium bicarbonate (3 × 20 mL), dried, and evaporated to give a mixture of **16** and **17**. These ketones were separated by gas chromatography on a 0.25 in. × 4 ft column of 10% OV-17 on Chromosorb W at 150 °C to yield 13 mg of **16** (retention time 17 min; IR (film) 2950, 2900, 2840, 1780, 1730, 1450, 1410, 1385, 1370, 1330, 1290, 1255, 1225, 1150, 1075, 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25–2.50 (5 H, m), 1.55 (6 H, s), 1.42 (3 H, s); MS, m/z 182 (M^+), 165, 141, 125, 93, 92) and 5 mg of **17**: (retention time 19.5 min; mp 35–37 °C; IR (film) 2990, 2940, 2890, 1780, 1730, 1450, 1420, 1390, 1380, 1350, 1320, 1290, 1250, 1210, 1160, 1120, 1060, 990; ^1H NMR ($CDCl_3$) δ 3.16 (1 H, d, J = 3 Hz), 3.05 (1 H, s), 2.55 (2 H, AB q, J = 10 Hz), 2.30 (1 H, m), 1.50 (3 H, s), 1.40 (3 H, s), 1.35 (3 H, s); MS, m/z 182 (M^+), 165, 125).

***exo*-7-[(*p*-Tolylsulfonyl)oxy]-1,5,5-trimethyl-4-oxabicyclo[4.2.0]octan-3-one (18).** A mixture of **14** and **15** (165 mg, 0.9 mmol), recrystallized *p*-toluenesulfonyl chloride (200 mg, 1.05 mmol), and 4-(dimethylamino)pyridine (5 mg) in dry pyridine (3 mL) was stirred at room temperature for 6 h. The mixture was poured into water and extracted with ether (3 × 30 mL), and the ethereal extract was washed with saturated aqueous sodium chloride. The organic layer was dried and evaporated, and the residue was subjected to preparative TLC. Development with 40% ethyl acetate in hexane, followed by elution with ethyl acetate, gave 200 mg (66%) of **18** as a viscous oil: IR (film) 2970, 2930, 2870, 1725, 1600, 1450, 1360, 1290, 1180, 1150, 1100, 1040, 1020, 990, 900, 860, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75 (2 H, d, J = 9 Hz), 7.30 (2 H, d, J = 9 Hz), 4.35 (1 H, d of t, J = 7, 1 Hz), 2.45 (5 H, br s), 2.20 (1 H, m), 2.05 (1 H, m), 1.35 (6 H, s), 1.17 (3 H, s). Anal. calcd for $C_{17}H_{22}O_5S$: C, 60.35; H, 6.55. Found: C, 59.98; H, 6.38.

***endo*-3-Hydroxy-*exo*-7-[(*p*-tolylsulfonyl)oxy]-1,5,5-trimethyl-4-oxabicyclo[4.2.0]octane (19).** To a stirred solution of **18** (80 mg, 0.24 mmol) in dichloromethane (5 mL) at −78 °C was added dropwise a 1 M solution of diisobutylaluminum hydride in hexane (0.24 mL, 0.24 mmol). After 1 h at −78 °C, the mixture was poured into saturated aqueous potassium tartrate (60 mL) and extracted with ethyl acetate (4 × 35 mL). The organic layer was washed with saturated aqueous sodium chloride (3 × 20 mL), dried, and evaporated to give 69 mg (85%) of virtually pure **19** as an oil: IR (film) 3400, 2970, 2940, 2880, 1600, 1450, 1360, 1240, 1220, 1180, 1120, 1100, 1050, 1020, 990, 960, 930, 900, 840, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.77 (2 H, d, J = 9 Hz), 7.35 (2 H, d, J = 9 Hz), 4.85 (1 H, br d, J = 9 Hz), 4.67 (1 H, q, J = 8 Hz), 3.70 (1 H, br, OH), 2.45 (3 H, s), 2.2–1.5 (5 H, m), 1.25 (3 H, s), 1.22 (3 H, s), 1.05 (3 H, s). Anal. Calcd for $C_{17}H_{22}O_5S$: C, 60.35; H, 6.55. Found: C, 59.94; H, 6.33.

(±)-Lineatin (1). To a stirred suspension of sodium hydride (50 mg, 10 mmol) of a 50% dispersion in mineral oil that had been washed with dry pentane) in ether (3 mL) was added a solution of **19** (30 mg, 0.09 mmol) in ether (1 mL). After stirring for 12 h at room temperature, the mixture was diluted with pentane and passed through silica gel (0.05 g). The solvent was removed by distillation at atmospheric pressure, and the residue was subjected to preparative gas-phase chromatography on a 0.25 in. × 4 ft column of 10% OV-10 on Chromosorb W at 125 °C to yield 10 mg (67%) of pure **1**: IR (CCl_4) 2950, 2925, 2860, 1450, 1380, 1360, 1340, 1315, 1240, 1220, 1180, 1170, 1120, 1100, 1075, 1010, 995, 960, 900 cm^{-1}; ^1H NMR (CCl_4) δ 4.90 (1 H, br d, J = 4 Hz), 4.37 (1 H, d of d, J = 5, 4 Hz), 1.98 (1 H, d, J = 5 Hz), 1.96 (1 H, d, J = 4 Hz), 1.82 (1 H, d, J = 4 Hz), 1.64 (2 H, br s), 1.19 (3 H, s), 1.18 (3 H, s), 1.13 (3 H, s); MS (CI), m/z 167, 149, 127. This material was indentical with an authentic sample of lineatin.

***endo*-3-Hydroxy-1,5,5-trimethyl-4-oxabicyclo[4.2.0]oct-7-ene (20).** To a stirred solution of **13** (80 mg, 0.50 mmol) in dichloromethane (4 mL) at −78 °C was added dropwise a 1 M solution of diisobutylaluminum hydride in hexane (0.5 mL, 0.5 mmol). After 1 h at −78 °C the mixture was poured into saturated aqueous sodium potassium tartrate (50 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed once with saturated aqueous sodium chloride, dried, and evaporated to give 76 mg (95%) of **20** as an oil, which was pure by TLC: IR (film) 3400, 2950, 1640, 1460, 1370, 1360, 1300, 1250, 1210, 1130, 1070, 1020, 760 cm^{-1}; [1]; ^1H NMR ($CDCl_3$) δ 6.08 (2 H, s), 5.25 (1 H, d of d, J = 9, 6 Hz), 3.75 (1 H, br, OH), 2.25 (1 H, s) 1.95 (2 H, t, J = 6 Hz), 1.33 (3 H, s), 1.25 (3 H, s), 1.17 (3 H, s); MS, m/z 151, 150, 127, 110, 109, 107, 96, 95. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.02; H, 9.36.

(±)-Isolineatin (2). A mixture of **20** (38 mg, 0.21 mmol) and mercuric pivalate (90 mg, 0.22 mmol) in tetrahydrofuran (2 mL) was stirred for 20 h at room temperature. A 1 M solution of sodium borohydride in 10% aqueous sodium hydroxide (1 mL) was added in one lot to the mixture, which was stirred for 10 min, poured into water, and extracted with pentane (3 × 25 mL). The pentane extract was washed once with saturated aqueous sodium chloride and dried, and the solvent was removed by distillation at atmospheric pressure. The residue was purified by preparative gas chromatography on a 0.25 in. × 4 ft column of OV-10 on Chromosorb W at 125 °C to give 16 mg (42%) of **2**: retention 2.6 min; IR (CCl_4) 2950, 2900, 2820, 1450, 1420, 1380, 1360, 1350, 1330, 1290, 1250, 1190, 1140, 1110, 1050, 1010, 850, 680 cm^{-1}; [1] H NMR (CCl_4) δ 5.27 (1 H, d, J = 3 Hz), 3.91 (1 H, t, J = 4 Hz), 2.50–1.75 (5 H, m), 1.40 (3 H, s), 1.25 (3 H, s), 1.09 (3 H, s); MS (CI); m/z 167, 151, 149, 137, 107. This material was identical with authentic isolineatin.

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Registry No. (±)-**1**, 71899-16-6; (±)-**2**, 71899-15-5; **5**, 20705-59-3; **6**, 80514-97-2; (±)-**7**, 674-26-0; **8**, 2381-87-5; (±)-**9**, 82795-65-1; (±)-**11**, 82740-90-7; (±)-**13**, 82740-91-8; (±)-**14**, 73671-77-9; (±)-**15**, 82740-92-9; (±)-**16**, 73671-78-0; (±)-**17**, 82268-30-2; (±)-**18**, 82740-93-0; (±)-**19**, 82740-94-1; (±)-**20**, 82740-95-2; ethyl acetate, 141-78-6; acetylene, 74-86-2.