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SYNTHESIS OF (1*S*:2*R*:4*S*:5*R*)-(−)-α-MULTISTRIATIN

THE PHEROMONE IN THE SMALLER EUROPEAN ELM BARK BEETLE, *SCOLYTUS MULTISTRIATUS*†

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Abstract—A synthesis of (−)-α-multistriatin was accomplished starting from D-mannitol. This established the absolute stereochemistry of the pheromone to be 1*S*:2*R*:4*S*:5*R*.

The bicyclic ketal α-multistriatin is one of three essential components of an aggregation pheromone for the European elm bark beetle, *Scolytus multistriatus* Marsham, which is the vector of Dutch elm disease in Europe and the United States.[1] Recently Silverstein *et al.* established the structure and relative stereochemistry of α-multistriatin as **1α** on the basis of chemical and spectrometric data.[2] They also showed it to be levorotatory and assigned (1*S*:2*R*:4*S*:5*R*)-absolute stereochemistry (**1α**).[3] In continuation of our work on the syntheses of optically active bicyclic ketal pheromones such as *exo*-brevicomin (**2**)[4] and frontalin (**3**),[5] a synthesis of α-multistriatin was undertaken to obtain an optically active form of known absolute configuration.

(*R*)-(+)-Glyceraldehyde acetonide (**4**) was chosen as the starting material, which was readily obtainable from D-mannitol.[6,7] The asymmetry at C-2 of this starting material was retained throughout the synthesis to give the optically active α-multistriatin. Addition of MeMgI to **4** yielded an epimeric mixture (57.5 and 27.3% as revealed by GLC) of alcohol **5** contaminated with two unidentified minor products (10.9 and 3.7%). This crude mixture was oxidized with the Jones CrO_3 to give a crude ketone (**6**). The Wittig reaction between **6** and methylene triphenylphosphorane gave an olefin (**7**), $[\alpha]_D^{23}$ +7.4° (C_6H_6). The optical purity of the olefin (**7**) was checked with the NMR optishift reagent, Eu(facam)$_3$,[8]‡ because the possibility of racemization during the Wittig reaction could not be excluded. Upon addition of Eu(facam)$_3$ the signals due to Me_2C and CH_2O remarkably shifted to lower field (0.3–0.4 ppm) and no sign of the contamination with the enantiomer was observable. This proved the high optical purity of the olefin (**7**). Hydroboration–oxidation of **7** yielded an epimeric mixture (50 and 37% as revealed by GLC) of alcohol **8a** contaminated with an unidentified minor by-product (13%). This was converted into the corresponding tosylate (**8b**). An iodide (**8c**) was prepared from **8b** in the usual manner.

The remaining task was the alkylation of diethyl ketone or its equivalent with **8b** or **8c**. An attempted alkylation of methyl 3-oxo-2-methylpentanoate with **8c** in the presence of NaOEt/EtOH§ resulted in the elimination of HI to give **7**. The alkylation of diethyl ketone with **8c** in the presence of $LiNPr_2^i$ in DME[9] gave the desired mono-alkylation product only in poor yield. The successful monoalkylation was achieved by the C-alkylation of the Mg salt of the cyclohexylimine (**9**) of diethyl ketone.[10]‖ Azeotropic removal of H_2O from a benzene soln of cyclohexylamine and diethyl ketone gave an oily imine (**9**). This was converted to the Mg salt by heating with MeMgBr in THF, which was subsequently reacted with **8b**. The resulting crude alkylation product was heated with dil HCl to effect hydrolytic removal of cyclohexylamine and acetone followed by intramolecular acetalization to give **1** via **10**. After chromatographic purification and distillation a mixture of multistriatin stereoisomers (**1**) was obtained in 40% yield from **8b**. GLC analysis showed that this was a mixture of all the four possible stereoisomers (**1α**:**1β**:**1γ**:**1δ** = 32.5:1.5:11:55). The separation of these isomers was accomplished by preparative GLC. The IR and NMR spectra of the separated isomers were identical with those reported for the corresponding racemates.[2] The distilled α-multistriatin (**1α**) with (1*S*:2*R*:4*S*:5*R*)-absolute stereochemistry was levorotatory: $[\alpha]_D^{23}$ −17.0° (ether). It should be added that the distilled (1*S*:2*S*:4*S*:5*R*)-δ-multistriatin (**1δ**) was also levorotatory: $[\alpha]_D^{23}$ −31.1° (ether). Finally, the optical purities of (−)-α-and (−)-δ-multistriatins were checked with the NMR optishift reagent, Eu(facam)$_3$. In the case of the (−)-α-isomer (**1α**), the observed down-field shifts of the Me signals and CH_2O signals were only *ca.* 0.1 and 0.2 ppm, respectively and no definite sign of the contamination with the (+)-enantiomer was observable in the spectrum. The (−)-δ-isomer (**1δ**) also seemed to be optically pure. Since the natural α-multistriatin was levorotatory,[3] the present synthesis unambiguously established the absolute stereochemistry of the pheromone to be 1*S*:2*R*:4*S*:5*R* as represented by **1α**.

In conclusion this work provided another illustration of the usefulness of a carbohydrate starting material in the synthesis of optically active natural products.¶

EXPERIMENTAL

All b.ps and m.ps were uncorrected. IR spectra refer to films and were determined on a Jasco IRA-1 spectrometer. NMR spectra were recorded at 60 MHz with TMS as an internal standard on a Hitachi R-24A spectrometer unless otherwise stated. Optical rotations were measured on a Jasco DIP-4 polarimeter. GLC analyses were performed on a Yanaco G 80 gas chromatograph. Preparative GLC was performed on a Hitachi K-53 gas chromatograph.

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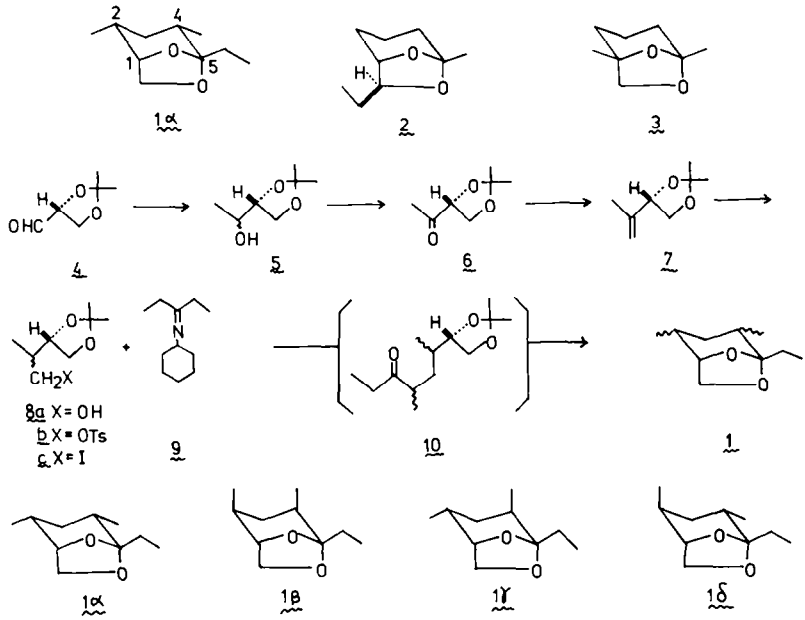
‡Tris[3 - (trifluoromethylhydroxymethylene) - d - camphorato] - europium (III).

§Cf. Ref. 4.

‖Cf. Refs. 1, 11.

¶Cf. Ref. 11.



(2R)-(+)-*Butane*-1,2,3-*triol* 1,2-*acetonide* (**5**). A soln of **4** (30 g) in dry ether (100 ml) was added dropwise at 0–15° to a stirred and ice-cooled soln of MeMgI prepared from Mg (20 g) and MeI (100 g) in dry ether (300 ml). After the addition the mixture was left to stand overnight at room temp and poured into ice-sat NH_4Cl soln. The ether layer was separated and the aqueous layer was extracted with EtOAc. The combined organic soln was washed with sat NaCl soln, dried (K_2CO_3) and concentrated *in vacuo*. The residue was distilled to give 23 g (50%) of **5**, b.p. 90–91°/20 mm, n_D^{23} 1.4308; $[\alpha]_D^{23}$ +26.5° (c = 2.15%, C_6H_6); ν_{max} 3440 (s), 2980 (s), 2940 (s), 2880 (s), 1460 (m), 1390 (s), 1380 (s), 1260 (s), 1220 (s), 1160 (m), 1065 (vs), 1000 (m), 960 (w), 910 (m), 850 (s), 795 (w) cm^{-1}; δ (CCl_4) 1.08 (1.2H, d, J = 7 Hz), 1.13 (1.8 H, d, J = 7 Hz), 1.28 (3H, s), 1.34 (3H, s), 2.82 (1H, –OH), 3.4–3.7 (4H, m). GLC (Column 10% Apiezon grease-L, 1.5 m at 100°; Carrier gas, N_2, 0.6 kg/cm²): Rt 3.9 min (27.3%), 4.5 min (57.5%), 5.7 min (10.9%), 7.6 min (3.7%). (Found: C, 57.40; H, 9.57. $C_7H_{14}O_3$ requires: C, 57.51; H, 9.65%).

(2R)-(+)-1,2-*Dihydroxybutan*-3-*one* 1,2-*acetonide* (**6**). The Jones CrO_3 reagent[12] (50 ml) was added dropwise at 0–10° to a stirred and ice-cooled soln of **5** (17 g) in acetone (500 ml). After the addition the mixture was stirred at 0–10° for 10 min. The excess CrO_3 was destroyed by the addition of MeOH and the acid was neutralized by the addition of $NaHCO_3$ powder. The acetone soln was separated from the solid by decantation and concentrated *in vacuo* in the presence of *ca.* 10 g of $NaHCO_3$. The residue was dissolved in ether. The ether soln was dried ($CaCl_2$) and concentrated *in vacuo*. The residue was distilled to give7.5 g (44%) of crude **6**, b.p. 70–75°/14 mm, n_D^{25} 1.4210; $[\alpha]_D^{23}$ +51.2° (c = 2.11%, C_6H_6); ν_{max} 3500 (w, probably due to impurities), 2990 (m), 2930 (m), 1805 (w, probably due to impurities), 1720 (s), 1450 (w), 1420 (w), 1380 (s), 1360 (m), 1265 (m), 1220 (s), 1150 (m), 1065 (s), 905 (w), 850 (s), 790 (w) cm^{-1}; δ (CCl_4) 1.32 (3H, s), 1.42 (3H, s), 2.18 (3H, s), 3.60–4.46 (3H, m). (Found: C, 56.45; H, 8.15. $C_7H_{12}O_3$ requires: C, 58.31; H, 8.39%). This unsatisfactory elemental analytical data may be due to contamination of some over-oxidation products. The Corey oxidation[13] resulted in incomplete reaction even with a great excess of the oxidant.

(2S)-(+)-3-*Methylbut*-3-*en*-1,2-*diol* 1,2-*acetonide* (**7**). Triphenylmethylphosphonium bromide (105 g) was added to a soln of $NaCH_2SOMe$ (from 14 g of 50% NaH) in dry DMSO (450 ml) under N_2 with stirring at room temp. The mixture was stirred for 10 min to yield an orange soln of the Wittig reagent. A soln of **6** (17.5 g) in dry ether (50 ml) was added dropwise to the stirred soln at 10–30°. The mixture was left to stand overnight at room temp, poured into ice water and extracted with ether. The ether soln was washed with sat NaCl soln, dried (K_2CO_3) and concentrated *in vacuo*. The residue was distilled to give 7.0 g (40%) of **7**, b.p. 68–72°/38 mm, n_D^{23} 1.4266; $[\alpha]_D^{23}$ +7.4° (c = 1.53%, C_6H_6); ν_{max} 3080 (w), 2990 (s), 2930 (m), 2880 (m), 1650 (w), 1450 (m), 1380 (s), 1250 (s), 1220 (s) 1160 (s), 1065 (s), 900 (m), 860 (s), 790 (w) cm^{-1}; δ (CCl_4) 1.30 (3H, s), 1.36 (3H, s), 1.70 (3H, s), 3.52 (1H, t, J = 8 Hz), 4.01 (1H, t, J = 8 Hz), 4.47 (1H, deformed t, J = 8 Hz), 4.95 (2H, d, J = 10 Hz); δ [7 (20 mg) + Eu(facam)₃ (80 mg) in 0.4 ml CCl_4] 1.60 (3H, s), 1.64 (3H, s), 1.81 (3H, s), 3.93 (1H, t, J = 8 Hz), 4.42 (1H, t, J = 8 Hz), 4.74 (1H, deformed t, J = 8 Hz), 5.06 (2H, d, J = 10 Hz). (Found: C, 67.64; H, 9.72. $C_8H_{14}O_2$ requires: C, 67.57; H, 9.93%).

(2S)-(+)-3-*Methylbutane*-1,2,4-*triol* 1,2-*acetonide* (**8a**). A THF soln of 0.8 M-B_2H_6 (60 ml) was added dropwise at 0–10° to a stirred and ice-cooled soln of **7** (14.0 g) in dry THF (50 ml) under N_2. After stirring for 2 hr at 0–5°, NaOH soln (4.0 g in 30 ml H_2O) and 30% H_2O_2 (30 ml) were added dropwise at 0–30° to the stirred and ice-cooled mixture. The stirring was continued for further 2 hr. The mixture was left to stand overnight at room temp and saturated with NaCl. The THF layer was separated and the aqueous layer was extracted with ether. The combined organic soln was washed with sat NaCl soln, dried (K_2CO_3) and concentrated *in vacuo*. The residue was distilled to give 12.5 g (80%) of **8a**, b.p. 88–103°/12 mm. An analytical sample boiled at 98–100°/12 mm, n_D^{23} 1.4380; $[\alpha]_D^{23}$ +4.3° (c = 2.68%, C_6H_6); ν_{max} 3440 (s), 2990 (s), 2940 (s), 2880 (s), 1460 (m), 1390 (s), 1380 (s), 1260 (s), 1230(s), 1160(s), 1070(s), 910(w), 860(s), 800(w) cm^{-1}; δ (CCl_4) 0.82 (1.2H, d, J = 7 Hz), 0.92 (1.8H, d, J = 7 Hz), 1.28 (3H, s) 1.30 (3H, s), 1.45–2.0 (1H, m), 3.12 (1H, s, –OH), 3.48 (2H, t, J = 6 Hz), 3.60–4.10 (3H, m). GLC (Column 10% Apiezon grease L, 1.5 m at 140°; Carrier gas, N_2, 0.65 kg/cm²): Rt 1.5 min (13%), 3.4 min (50%), 3.8 min (37%). (Found: C, 59.63; H, 9.92. $C_8H_{16}O_3$ requires: C, 59.98; H, 10.07%).

(2S)-3-*Methylbutane*-1,2,4-*triol*-1,2-*acetonide*-4-*tosylate* (**8b**). Powdered *p*-TsCl (8.0 g) was added to an ice-cooled and stirred soln of **8a** (4.8 g) in dry C_5H_5N (25 ml). The mixture was left to stand overnight in a refrigerator, poured into ice-water and extracted with ether. The ether soln was washed with $CuSO_4$ soln to remove C_5H_5N, water, $NaHCO_3$ soln and sat NaCl soln, dried ($MgSO_4$) and concentrated *in vacuo* to give crude oily **8b** (11 g, quantitative), ν_{max} 2950 (s), 1600 (m), 1370 (s), 1200 (s) 1180 (s), 1100 (m), 1070 (m), 970 (m), 860 (m), 835 (m), 820 (m), 795 (m), 670 (m) cm^{-1}; δ (CCl_4) 0.90 (1.8 H, d, J = 7 Hz), 0.95 (1.2H, d, J = 7 Hz), 1.25 (6H, br. s), 2.46 (3H, s), 3.30–4.20 (5H, m), 7.35 (2H, d, J = 9 Hz), 7.82 (2H, d, J = 9 Hz). This was employed for the next step without further purification.

(2S)-4-*Iodo*-3-*methylbutane*-1,2-*diol acetonide* (**8c**). A soln of **8b** (27.0 g) and LiI (22 g) in acetone (350 ml) was stirred and heated

under reflux for 5 hr. The mixture was concentrated *in vacuo*. The residue was dissolved in H_2O and extracted with ether. The ether soln was washed with water and sat NaCl soln, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 15.0 g (71%) of **8c**, b.p. 85–93°/8 mm. An analytical sample boiled at 90°/8 mm, n_D^{23} 1.4616; $[\alpha]_D^{23}$ −4.3° (*c* = 2.04%, C_6H_6); ν_{max} 2995 (s), 2940 (m), 2880 (m), 1460 (m), 1390 (s), 1380 (s), 1260 (m), 1230 (s), 1160 (m), 1070 (vs), 1000 (m), 915 (w), 860 (m), 800 (w) cm^{-1}. (Found: C, 36.01; H, 5.63. $C_8H_{15}O_2I$ requires: C, 35.57; H, 5.59%).

Cyclohexylimine of pentan-3-one (**9**). Azeotropic removal of H_2O from a refluxing benzene soln of cyclohexylamine and pentan-3-one gave an oily **9**, b.p. 110°/30 mm, n_D^{22} 1.4623; ν_{max} 2980 (s), 2940 (s), 2860 (s), 2660 (w), 1725 (w), 1665 (vs), 1460 (s), 1380 (m), 1185 (w), 1120 (w), 1025 (w), 960 (m), 940 (w), 890 (m), 850 (w), 800 (w) cm^{-1}; δ (CCl_4) 0.98 (6H, t, J = 7 Hz), 1.2–1.9 (10H), 2.15 (4H, q, J = 7 Hz), 3.28 (1H, br). (Found: C, 78.42; H, 12.19; N, 8.40. $C_{11}H_{21}N$ requires: C, 78.97; H, 12.65; N, 8.37%).

A mixture of multistriatin stereoisomers (**1**). A soln of **9** (8 g) in dry THF (15 ml) was added to a stirred soln of EtMgBr prepared from Mg (1.2 g) and EtBr (6 g) in dry THF (20 ml) under N_2. The mixture was stirred and heated under reflux for 3 hr (C_2H_6 evolution) and cooled. This caused the precipitation of the Mg salt. A soln of **8b** (11 g) in dry THF (20 ml) was added to the ice-cooled and stirred mixture at 0–5°. Then the mixture was stirred and heated under reflux for 2 hr when the soln became turbid. Subsequently THF was removed *in vacuo* and the residue was treated with dil HCl (10 ml of conc HCl and 50 ml of H_2O). At the end of the exothermic reaction the mixture was stirred and heated at 50–60° for 30 min. After cooling, the soln was saturated with NaCl and extracted with ether. The ether extract was washed with H_2O, sat $NaHCO_3$ soln and sat NaCl soln, dried (K_2CO_3) and concentrated *in vacuo*. The residue (*ca.* 5 g) was chromatographed over alumina (Woelm, neutral, grade II, 70 g, 10 × 3.2 cm) in light petroleum. Elution with light petroleum yielded 2.0 g (40%) of **1**, b.p. 104–108°/40 mm, n_D^{22} 1.4497; $[\alpha]_D^{22}$ −27.0° (*c* = 1.3%, ether); ν_{max} 2980 (s), 2940 (s), 2880 (s), 1490 (w), 1460 (m), 1380 (m), 1365 (m), 1330 (w), 1315 (w), 1290 (w), 1255 (m), 1200 (m), 1180 (m), 1135 (m), 1120 (m), 1080 (w), 1050 (s), 1035 (s), 990 (m), 980 (m), 960 (m), 915 (s), 900 (s), 820 (w), 770 (w) cm^{-1}; δ (CCl_4) 0.6–2.0 (15H, 0.72, 0.75, 0.83, 0.88, 0.99, 1.08, 1.18, 1.35, 1.47, 1.58, 1.70, 1.82), 3.40–3.95 (2H, 3.50, 3.60, 3.73, 3.79, 3.90), 4.15 (1H, br. s). GLC (Column, 10% PEG 20M on Celite 545 (2m × 2 cm i.d.) at 90°; Carrier gas, N_2, 1.5 kg/cm^2): Rt 9.6 min (55%, 1δ), 10.4 min (32.5% 1α), 11.2 min (11%, 1γ), 12.6 min (1.5%, 1β). (Found: C, 70.82; H, 10.46. $C_{10}H_{18}O_2$ requires: C, 70.54; H, 10.66%).

Separation of the multistriatin stereoisomers and their properties. The separation was carried out using a glass column (2m × 2 cm i.d.) packed with 10% PGE 20 M on Celite 545 at 90° with N_2 as the carrier gas (1.5 kg/cm^2).

(1S:2R:4S:5R)-(−)-*α-multistriatin* (**1α**). This boiled at 85–100° (bath temp)/31 mm to give 119 mg of **1α**, n_D^{23} 1.4488; $[\alpha]_D^{23}$ −17.0° (*c* = 0.554%, ether); ν_{max} 2960 (vs), 2930 (vs), 2880 (s), 1485 (m), 1460 (s), 1440 (sh, m), 1385 (m), 1365 (m), 1340 (w), 1320 (w), 1290 (m), 1255 (s), 1210 (m), 1180 (s), 1160 (m), 1130 (s), 1095 (m), 1055 (sh, m), 1035 (vs), 1000 (w), 990 (m), 955 (m), 920 (s), 895 (s), 820 (w), 790 (w), 760 (w) cm^{-1}; δ (100 MHz, $CDCl_3$) 0.81 (6H, d, J = 7 Hz), 0.92 (3H, t, J = 7 Hz), 1.4–2.2 (6H, m, 1.68, 2H, q, J = 7 Hz), 3.68 (1H, dd, J_1 = 4, J_2 = 8 Hz), 3.85 (1H, d, J = 8 Hz), 4.14 (1H, m); δ (60 MHz, $CDCl_3$) 0.80 (6H, d, J = 7 Hz), 0.92 (3H, t, J = 7 Hz), 1.1–2.3 (6H, m), 3.67 (1H, dd, J_1 = 4, J_2 = 8 Hz), 3.89 (1H, d, J = 8 Hz), 4.23 (1H, m); δ [60 MHz, **1α** (20 mg) + Eu(facam)$_3$ (80 mg) in 0.4 ml $CDCl_3$] 0.85 (6H, d, J = 7 Hz), 0.98 (3H, t, J = 7 Hz), 3.83 (1H, dd, J_1 = 4, J_2 = 8 Hz), 4.04 (1H, d, J = 8 Hz), 4.35 (1H, m). MS (70 eV): *m/e* 27.0227 (C_2H_3, 14%), 29.0393 (C_2H_5, 38%), 39.0277 (C_3H_3, 14%), 41.0428 (C_3H_5, 26%), 43.0216 (C_2H_3O, 14%), 54.0472 (C_4H_6, 14%), 55.0541 (C_4H_7, 42%), 57.0343 (C_3H_5O, 100%), 71.0498 (C_4H_7O, 34%), 81.0715 (C_6H_9, 22%), 96.0963 (C_7H_{12}, 42%), 128.0836 ($C_7H_{12}O_2$, 26%), 170.1326 ($C_{10}H_{18}O_2 = M^+$, 4%). (1S:2S:4R:5R)-*β-multistriatin* (**1β**). This could not be distilled, since the yield was only 35 mg; ν_{max} 2980 (vs), 2940 (vs), 2880 (vs), 1720 (m, impurity ?), 1485 (m), 1470 (s), 1385 (s), 1370 (m), 1340 (w), 1320 (m), 1310 (w), 1290 (w), 1275 (w), 1260 (m), 1240 (m), 1200 (s), 1190 (m), 1170 (s), 1150 (m), 1130 (m), 1110 (m), 1090 (w), 1060 (vs), 1040 (s), 1025 (s), 1010 (s), 990 (m), 980 (s), 960 (m), 910 (s), 900 (s), 820 (w), 780 (w), 760 (m), 700 (w) cm $^{-1}$; δ (60 MHz, $CDCl_3$) 0.92 (3H, t, J = 7 Hz), 1.10 (3H, d, J = 7 Hz), 1.23 (3H, d, J = 7 Hz), 1.5–2.6 (6H, m), 3.88 (2H, seemingly d, J = 3 Hz) 4.30 (1H, br. s). (1S:2R:4R:5R)-γ-*multistriatin* (**1γ**). This could not be distilled, since the yield was only 65 mg; ν_{max} 2960 (vs), 2930 (vs), 2880 (vs), 1485 (m), 1470 (s), 1380 (m), 1370 (sh, m), 1360 (m), 1350 (w), 1330 (w), 1300 (w), 1285 (w), 1250 (m), 1240 (w), 1200 (m), 1180 (s), 1170 (s), 1140 (m), 1130 (m), 1110 (m), 1085 (w), 1070 (w), 1050 (s), 1040 (vs), 1020 (vs), 995 (m), 985 (m), 975 (m), 960 (m), 950 (m), 905 (vs), 820 (w), 780 (w), 760 (w), 750 (w) cm $^{-1}$; δ (60 MHz, $CDCl_3$) 0.82 (3H, d, J = 7 Hz), 0.94 (3H, t, J = 7 Hz), 1.02 (3H, d, J = 7 Hz), 1.2–2.5 (6H, m), 3.70 (1H, dd, J_1 = 5, J_2 = 7 Hz), 3.98 (1H, seemingly d, J = 7 Hz), 4.25 (1H, m). (1S:2S:4S:5R)-(−)-*δ-multistriatin* (**1δ**). The fraction obtained by preparative GLC boiled at 85–100° (bath temp)/31 mm to yield 165 mg of **1δ**, n_D^{23} 1.4488; $[\alpha]_D^{23}$ −31.1° (*c* = 0.745%, ether); ν_{max} 2970 (vs), 2930 (vs), 2880 (s), 1485 (m), 1460 (s), 1380 (m), 1365 (m), 1330 (w), 1310 (w), 1310 (w), 1285 (w), 1250 (s), 1200 (s), 1170 (m), 1145 (w), 1130 (m), 1115 (m), 1050 (vs), 1020 (m), 990 (s), 980 (s), 955 (m), 910 (s), 895 (s), 860 (w), 820 (w), 765 (w), cm $^{-1}$, δ (100 MHz, $CDCl_3$) 0.78 (3H, d, J = 7 Hz), 0.90 (3H, t, J = 7 Hz), 1.13 (3H, d, J = 7 Hz), 1.2–2.2 (6H, m), 3.82 (2H, seemingly d, J = 3 Hz), 4.22 (1H, m); δ (60 MHz, $CDCl_3$) 0.82 (3H, d, J = 7 Hz), 0.95 (3H, t, J = 7 Hz), 1.16 (3H, d, J = 7 Hz), 1.2–2.2 (6H, m), 3.88 (2H, seemingly d, J = 3 Hz), 4.28 (1H, m); δ [60 MHz, **1δ** (20 mg) + Eu(facam)$_3$ (80 mg) in 0.4 ml $CDCl_3$] 0.85 (3H, d, J = 7 Hz), 0.99 (3H, t, J = 7 Hz), 1.18 (3H, d, J = 7 Hz), 3.96 (2H, seemingly d, J = 3 Hz), 4.33 (1H, m). MS (70 eV): *m/e* 27.0223 (C_2H_3, 30%), 28.0311 (C_2H_4, 26%), 29.0393 (C_2H_5, 76%), 39.0265 (C_3H_3, 26%), 41.0421 (C_3H_5, 44%), 42.0492 (C_3H_6, 12%), 53.0388 (C_4H_5, 12%), 54.0461 (C_4H_6, 26%), 55.0536 (C_4H_7, 56%), 57.0329 (C_3H_5O, 100%), 58.0371 (C_3H_6O, 12%), 71.0484 (C_4H_7O, 24%), 81.0700 (C_6H_9, 38%), 86.0725 ($C_5H_{10}O$, 16%), 96.0923 (C_7H_{12}, 36%), 128.0815 ($C_7H_{12}O_2$, 22%), 170, 1312 ($C_{10}H_{18}O_2 = M^+$, 11%).

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