Supporting Information

A Short Stereoselective Total Synthesis of the Fusarium Toxin Equisetin

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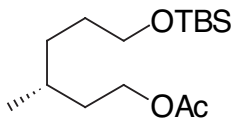
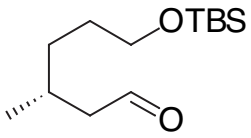
(*R*)-(+)-1-(*tert*-Butyl-dimethyl-silanyloxy)-6-acetoxy-4-methyl-hexane



4

$[\alpha]_D^{30}$ +7.7° (*c* 1.03, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 2955s, 2859s, 2872m, 1743s (OC=O), 1472, 1388, 1366, 1248s, 1098s, 1034, 938, 836s, 775m; δ_H 4.04-4.03 (2H, m, $C\underline{H}_2OCOCH_3$), 3.53 (2H, t, *J* 6.0, $C\underline{H}_2OSi$), 1.98 (3H, s, $COC\underline{H}_3$), 1.62-1.12 (7H, m, 3 x $C\underline{H}_2$ and $C\underline{H}CH_3$), 0.86 (3H, d, *J* 10.6, $CHC\underline{H}_3$), 0.84 (9H, s, $SiC(C\underline{H}_3)_3$), -0.01 (6H, s, $Si(C\underline{H}_3)_2$); δ_C 171.0, 63.3, 62.9, 35.5, 32.9, 30.1, 29.6, 25.9, 20.9, 19.4, 18.3, -5.4; *m/z* (EI^+) 289 (68%, MH^+), 231 (100%), 171 (51%), 117 (94%). [Found (EI^+): MH^+, 289.2200. $C_{15}H_{32}SiO_3$ MH^+ requires, 289.2199].

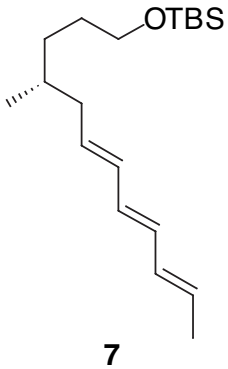
(*R*)-(+)-1-(*tert*-Butyl-dimethyl-silanyloxy)-3-methyl-hexanal



5

$[\alpha]_D^{30}$ +12.6° (*c* 1.04, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 2955s, 2930s, 2883s, 2857s, 1728s (C=O), 1475, 1462, 1387, 1361, 1255s, 1097s, 1006, 938, 836s, 813, 775s; δ_H 9.74 (1H, s, $C\underline{H}O$), 3.58 (2H, t, *J* 6.4, $C\underline{H}_2OSi$), 2.42-2.01 (2H, m, CH_2CO), 1.58-1.20 (5H, m, 2 x $C\underline{H}_2$ and $C\underline{H}CH_3$), 0.95 (3H, d, *J* 6.7, $CHC\underline{H}_3$), 0.87 (9H, s, $SiC(C\underline{H}_3)3$), 0.03 (6H, s, $Si(CH_3)_2$); δ_C 202.9, 63.1, 51.0, 33.0, 30.2, 28.0, 25.9, 19.9, 18.3, -5.3; *m/z* (EI^+) 243 (28%, M^+), 203 (87%), 185 (100%). [Found (EI^+): M^+, 244.1871. $C_{13}H_{28}SiO_2$ M^+ requires, 244.1859].

(6*E*,8*E*,10*E*)-(*R*)-(+)-(*tert*-Butyl-dimethyl-silanyloxy)-4-methyl- dodeca-6,8,10-triene

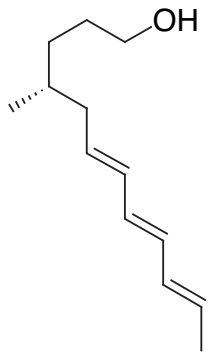


7

$[\alpha]_D^{30}$ -0.50° (*c* 1.00, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 3013m, 2953s, 2928s, 2856s, 1684, 1652, 1471, 1462, 1377, 1360, 1254s, 1097s, 994s, 938s, 835s, 813, 775s; δ_H 6.09-5.99 (4H, m, $C\underline{H}C\underline{H}C\underline{H}C\underline{H}CHCH_3$), 5.71-5.63 (1H, m, $CH(CH)_4C\underline{H}CH_3$), 5.63 (1H, dt, *J* 14.2 and 7.4, $C\underline{H}(CH)_4C\underline{H}CH_3$), 3.60-3.56 (2H, t, *J* 6.7, $C\underline{H}_2OSi$), 2.09 (1H, dt, *J* 14 and 7.5, $CHC\underline{H}HCH$), 1.93 (1H, dt, *J* 14 and 7.5, $CHCH\underline{H}CH$), 1.76 (3H, d, *J* 6.6, $CHCHC\underline{H}_3$), 1.59-1.43 and 1.39-1.25 and 1.17-1.05 (5H, m, $C\underline{H}_2CH_2OSi$, $C\underline{H}_2CH_2CH_2OSi$ and $C\underline{H}(CH_3)CH_2$), 0.89 (9H, s, $SiC(C\underline{H}_3)_3$), 0.87 (3H, d, *J* 6.7, $CHC\underline{H}_3CH_2$), 0.05 (6H, s, $Si(CH_3)_2$); δ_C 131.9, 131.7, 130.8, 130.6, 128.6, 125.9, 63.5, 40.3, 33.2, 32.7, 30.5, 26.0,

19.6, 18.3, 18.2, -5.3; *m/z* (EI^+) 308 (20%, M^+), 251 (100%,). [Found (EI^+): M^+, 308.2560. $C_{19}H_{36}SiO$ M^+ requires, 308.2535].

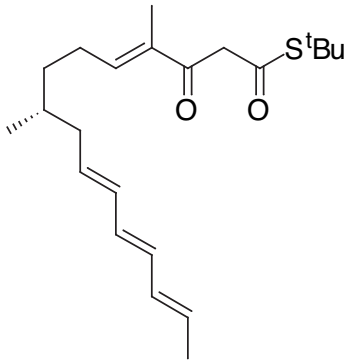
(6*E*,8*E*,10*E*)-(*R*)-(+)-4-methyl-dodeca-6,8,10-triene-1-ol



8

$[\alpha]_D^{30}$ −1.05° (*c* 0.57, $CHCl_3$); ν_{max}(Nujol mull)/cm^{-1} 3362m (OH), 2924s, 2854s, 1680, 1652, 1459s, 1377m, 1275, 1089, 1050, 994, 880; δ_H 6.10-6.02 (4H, m, C<u>H</u>C<u>H</u>C<u>H</u>C<u>H</u>CHCH$_3$), 5.71-5.59 (2H, m, C<u>H</u>(CH$_2$)$_4$C<u>H</u>CH$_3$), 3.62 (2H, dd, *J* 12.0 and 6.4, C<u>H</u>$_2$OH), 2.14-2.07 and 1.99-1.91 (2H, m, CHC<u>H</u>$_2$CH), 1.76 (3H, d, *J* 6.7, CHCHC<u>H</u>$_3$), 1.65-1.12 (6H, m, C<u>H</u>$_2$CH$_2$OH, C<u>H</u>$_2$CH$_2$CH$_2$OH, C<u>H</u>(CH$_3$)CH$_2$ and O<u>H</u>), 0.89 (3H, d, *J* 6.7, CHC<u>H</u>$_3$CH$_2$); δ_C 132.6, 131.7, 131.6, 130.9, 130.5, 128.9, 63.3, 40.3, 33.2, 32.5, 30.4, 19.5, 18.2; *m/z* (EI^+) 194 (78%, M^+), 107 (85%), 94 (54%), 79 (100%). [Found (EI^+): M^+, 194.1667. $C_{13}H_{22}O$ M^+ requires, 194.1671].

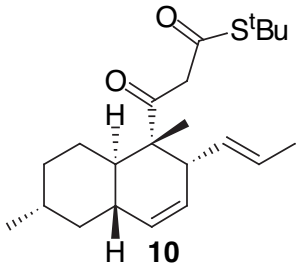
(4*E*,10*E*,12*E*,14*E*)-(*R*)-(+)-4,8-Dimethyl-3-oxo-hexadeca-4,10,12,14-tetraenethioic acid *S-tert*-butyl ester



2

In $CDCl_3$ at room temperature the title compound exists as a (10:3) *keto:enol* mixture. ν_{max}(thin film)/cm^{-1} 3013m, 2962s, 2926s, 1693s, 1661s, 1643s, 1584s, 1455m, 1375m, 1364m, 1295, 1161, 1100s, 1063s, 996s; δ_H 6.62 (1H, t, *J* 6.7, C<u>H</u>C(CH$_3$)CO *keto-form*), 6.55 (1H, t, *J* 7.1, C<u>H</u>C(CH$_3$)COH *enol-form*), 6.07-6.02 (4H, m, C<u>H</u>C<u>H</u>C<u>H</u>C<u>H</u>CHCH$_3$), 5.69-5.57 (2H, m, C<u>H</u>(CH$_2$)$_4$C<u>H</u>CH$_3$), 5.49 (1H, s, C(OH)C<u>H</u>CO *enol*), 3.82 (2H, s, COCH$_2$CO *keto*), 2.32-1.91 (4H, m, C<u>H</u>$_2$CHC(CH$_3$)CO and CH$_3$CHC<u>H</u>$_2$CHCH), 1.77 (3H, d, *J* 7.3, CHCHC<u>H</u>$_3$), 1.75 (3H, s, CHC(C<u>H</u>$_3$)CO *keto*), 1.72 (3H, s, CHC(C<u>H</u>$_3$)COH *enol*), 1.52 (9H, s, C(CH$_3$)$_3$ *keto*), 1.46 (9H, s, C(C<u>H</u>$_3$)$_3$ *enol*), 1.30-1.18 (3H, m, C<u>H</u>$_2$CH$_2$CHC(CH$_3$)CO and C<u>H</u>(CH$_3$)CH$_2$), 0.89 (3H, d, *J* 6.7, CHC<u>H</u>$_3$CH$_2$); δ_C(*keto-form*) 193.4, 193.2, 145.9, 137.0, 132.2, 131.9, 131.7, 131.1, 130.3, 129.0, 53.8, 48.8, 40.1, 35.0, 33.0, 29.6, 27.0, 19.4, 18.2, 11.3; *m/z* (EI^+) 362 (30%, M^+), 305. (26%), 203 (100%), 174 (94%), 107 (70%). [Found (EI^+): M^+, 362.2264. $C_{22}H_{34}SO_2$ M^+ requires, 362.2279].

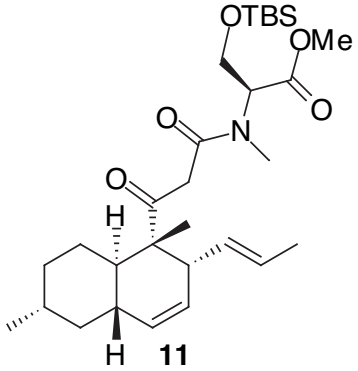
3-(1,6-Dimethyl-2-propenyl-1,2,4a,5,6,7,8,8a-octahydro-naphthalen-1-yl)-3-oxo-thiopropionic acid *S-tert*-butyl ester



10

In $CDCl_3$ at room temperature the title compound exists as a (10:3) *keto:enol* mixture. $[\alpha]_D^{30}$ −139° (*c* 0.26, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 3015m, 2949s, 2913s, 2867, 1716s, 1682s, 1652, 1599s, 1558, 1540, 1456s, 1394m, 1375m, 1384m, 1287, 1215, 1162, 1075s, 1044m, 975, 962, 923, 860, 832, 776, 753; δ_H 5.43-5.29 (3H, m, C<u>H</u>=C<u>H</u> of octalin and CH=C<u>H</u>CH_3), 5.13 (1H, ddq, *J* 15.1, 9.4 and 1.4, C<u>H</u>=$CHCH_3$), 3.62 (1H, d, *J* 15.5, COC<u>H</u>HCO), 3.46 (1H, s, *J* 15.5, COCH<u>H</u>CO), 2.54-2.52 (1H, m, C<u>H</u>CH=$CHCH_3$), 2.40-2.38 (1H, m, C<u>H</u>CH=$CHCH_3$ *enol*), 1.80-1.77 (1H, m, $CH_3CHC\underline{H}_{eq}H_{ax}CH$), 1.75-1.65, (3H, m, $CH_3CHCH_2C\underline{H}_{ring\ junc.}$, $CH_3CHCH_2CH_{eq}\underline{H}_{ax}CH$ and $CH_3CHC\underline{H}_{eq}H_{ax}CH$), 1.67-1.60 (2H, obscured m, $CH_3C\underline{H}CH_2CH$ and $CH_3CHCH_2CH_2C\underline{H}_{ring\ junc.}$), 1.62 (3H, dd, *J* 6.5 and 1.4, CH=CHC<u>H</u>$_3$), 1.51 (s, 9H, SC(C<u>H</u>$_3$)$_3$ *enol*), 1.46 (s, 9H, SC(C<u>H</u>$_3$)$_3$ *keto*), 1.22-0.99 (1H, m, $CH_3CHCH_2C\underline{H}_{eq}H_{ax}CH$), 1.17 (3H, s, C<u>H</u>$_3$CCO *keto*), 1.05 (3H, s, C<u>H</u>$_3$CCO *enol*), 0.96-0.89 (1H, m, $CH_3CHCH_{eq}\underline{H}_{ax}CH_2$), 0.90 (3H, d, *J* 6.6, C<u>H</u>$_3$CHCH$_2$CH), 0.86 (1H, d, *J* 12.1, $CH_3CHCH_{eq}\underline{H}_{ax}CH$); δ_C 205.0, 193.1, 181.0, 131.7, 130.6, 130.5, 130.0, 127.5, 126.9, 126.4, 125.2, 99.6, 54.7, 53.5, 49.5, 48.6, 41.9, 39.7, 38.3, 35.5, 33.3, 29.7, 27.2, 22.4, 17.8, 16.8; *m/z* (EI$^+$) 362 (71%, M$^+$). [Found (EI$^+$): (M$^+$-57), 305.1589. ($C_{22}H_{34}SO_2$ M$^+$-57) requires, 305.1572].

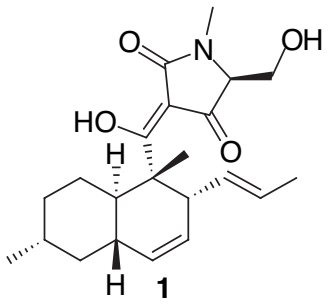
3-(*tert*-Butyl-dimethyl-silanyloxy)-2-{[3-(1,6-dimethyl-2-propenyl-1,2,4a,5,6,7,8,8a-octahydro-naphthalen-1-yl)-3-oxo-propionyl]-methyl-amino}-propionic acid methyl ester



11

In $CDCl_3$ at room temperature the title compound exists as a (5:2) *keto:enol* mixture. The ^{1}H NMR is complicated further by the presence of a mixture of amide rotamers. δ_H 5.41-5.36 and 5.29-5.08 (4H, m, C<u>H</u>C<u>H</u>CH$_3$ and CHC<u>H</u>C<u>H</u>CHC(CH$_3$) and *enolic* COC<u>H</u>COH), 4.39 (1H, m, N(CH$_3$)C<u>H</u>), 4.15-4.11 and 4.01-3.97 (2H, 2 × m, C<u>H</u>$_2$OSi), 3.75 (1H, d, *J* 15.8, COCH<u>H</u>CO), 3.71 (3H, s, OC<u>H</u>$_3$) 3.38 (1H, d, *J* 15.8, COC<u>H</u>HCO), 3.08-3.06 (3H, m, NC<u>H</u>$_3$), 2.60-2.52 (1H, m, C<u>H</u>CH=$CHCH_3$), 2.42-2.40 (1H, m, C<u>H</u>CH=$CHCH_3$ *enol*), 1.81-1.58, 1.47-1.43, 1.26-1.22 and 1.12-0.86 (9H, 4 × m, saturated protons of octalin ring), 1.60 (3H, d, *J* 6.2, CHCHC<u>H</u>$_3$), 1.22 (3H, s, CHC(C<u>H</u>$_3$)CO), 0.90 (3H, m, $CH_2CH_2CH(C\underline{H}_3)$), 0.87 (9H, s, SiC(C<u>H</u>$_3$)$_3$), 0.06 (6H, s, Si(C<u>H</u>$_3$)$_2$); [Found (ES$^+$): (M$^+$+Na), *m/z* 542.3289. ($C_{29}H_{49}SiO_5$ M$^+$ + Na) requires, 542.3278].

Equisetin



1

$[\alpha]^{28}_{D}$ = -262 (c 0.038, $CHCl_3$); ν_{max} (film) 2923, 2854, 1602, 1453 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 (br s, 2H), 5.30-5.10 (m, 2H), 4.03 (dd, *J* 11.5, 3.7, 1H), 3.95-3.82 (m, 1H), 3.64 (t, *J* 4.4, 1H), 3.32 (br s, 1H), 3.06 (s, 3H), 2.10-1.65 (m, 4H), 1.56 (d, *J* 4.8, 3H), 1.60-1.40 (m, 7H), 1.30-0.90 (m, 3H), 0.92 (d, *J* 6.5, 3H); *m*/*z* (ES^+) 374 (100%), 356 (15%); [Found *m*/*z* (ES^+) 396.2148. $C_{22}H_{31}O_4NNa$ requires 396.2151].