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Facile Synthesis of (-)-Serricornin by Means of Palladium-Catalyzed Hydrogenolysis of Alkenyloxiranes

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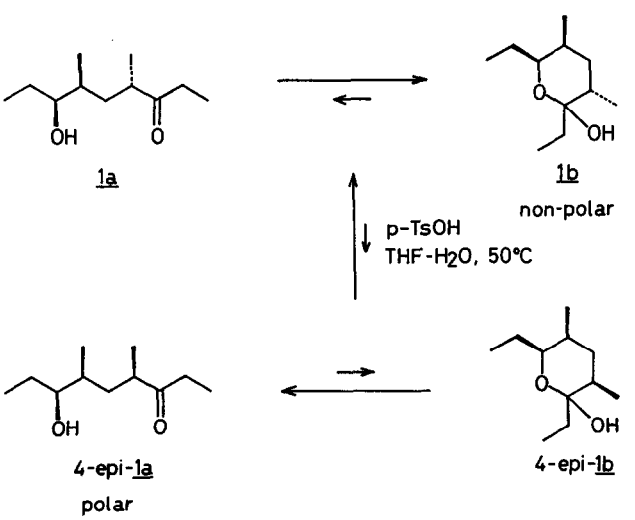
Chiral synthesis of (-)-serricornin by using palladium-catalyzed stereoselective hydrogenolysis of the alkenyloxirane to the homoallylic alcohol with formic acid as a key step was carried out.

Introduction

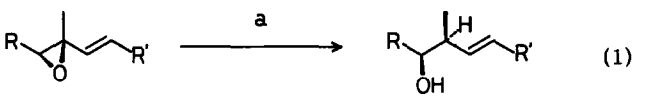
(-)-Serricornin **1** is a sex pheromone produced by *Lasioderma serricorne F.*, a female cigarette beetle, which is a serious pest of cured tobacco leaves.[1] The structure of serricornin was determined as (4*S*,6*S*,7*S*)-7-hydroxy-4,6-dimethyl-3-nonanone **1a** by Mori.[2] Although several syntheses of 1 have been reported, they require somewhat tedious steps from easily available starting materials.[3] Development of much more convenient synthetic methods for 1 is current expectancy for the sake of the practical use.



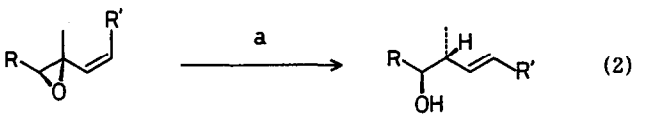
Scheme 1

Mori and co-workers have reported that serricornin and its C-4 epimer are easily separatable by chromatography on account of the free energy difference in the equilibrium between the acyclic form **1a** and the less polar cyclic forms **1b** (Scheme 1). In addition the C-4 epimer can be converted to serricornin by acid catalyzed isomerization.[4] Considering these information, the most significant step for the synthesis of serricornin 1 is focused upon enantio- and diastereoselective construction of vicinal chiral centers of 6*S* and 7*S* carbons and stereochemistry of C-4 is considered to be strategically negligible.

Recently we have developed a useful synthetic method for preparation of acyclic compounds which have hydroxy and methyl groups on vicinal carbons by stereospecific hydrogenolysis of 4-methyl-4,5-epoxy-2-alkenoates **2** with formic acid using palladium-catalyst (R=H in Scheme 3).[5] We have also found that the selectivity of hydride attack to the oxirane depends on the substituents of olefins. Thus, hydrogenolysis of alkenyloxiranes having *trans*-olefins proceeds with inversion of configuration at oxirane carbon (eq. 1). On the other hand, retention of configuration and olefin isomerization take place simultaneously in the reaction of those having *cis*-olefins (eq. 2). However no example of trisubstituted olefins has been reported.



(1)

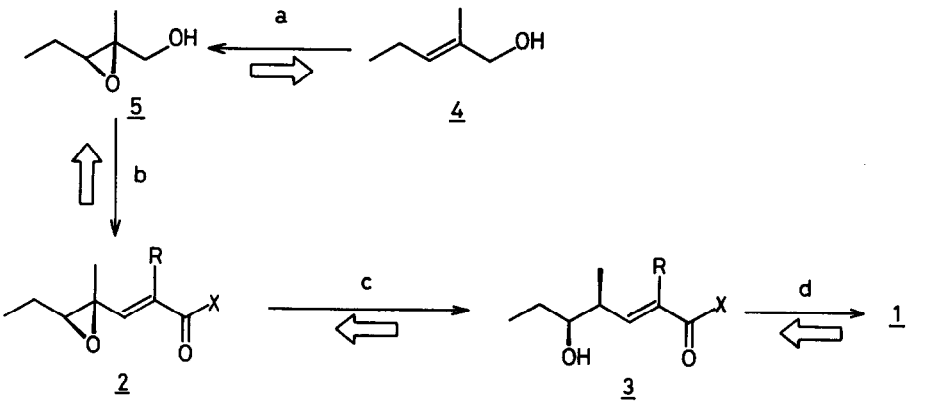


(2)

[a] $Pd_2(dba)_3CHCl_3$ (2.5 mol%), P^nBu_3 (2.5 mol%), HCO_2H (5 equiv.), Et_3N (2 equiv.), dioxane, r.t., 78-97%.

Scheme 2

We have thought that if the 2-methylated analogue of the epoxy unsaturated ester, **2b**, or the ketone **2c** can be similarly converted to the syn isomer **3b** or **3c** by the palladium-catalyzed hydrogenolysis, the method is efficiently applicable to the synthesis of (-)-serricornin 1, because chiral oxirane **5** are easily available from 2-methyl-2-pentenol **4** using chiral epoxidation catalyzed by $Ti(O^iPr)_4$-(+)-DET.[6] For the synthesis of (-)-serricornin we have studied the selectivity of hydrogenolysis of **2b** as shown in our synthetic approach (Scheme 3). A compound related to the expected product **3b** from the ester **2b** is known as an intermediate of the synthesis of (-)-serricornin 1.[3f] We have also studied selectivity of the hydrogenolysis of the γ,δ-epoxy-α,β-unsaturated ketone **2c** to the hydroxy unsaturated ketone **3c**. The latter provides a short convenient synthesis of (-)-serricornin 1.



2a: R = H, X = OEt, 63%
2b: R = Me, X = OEt, 84%
2c: R = Me, X = Et, 48%

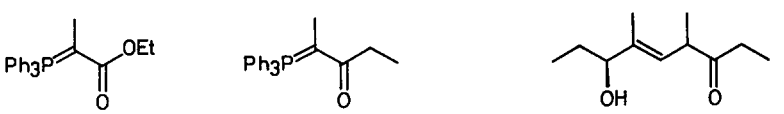
3a: 85%
3b: 90%
3c: 48% (35% of **2c** was recovered)

[a]$Ti(O^iPr)_4$, (+)-DET, ^tBuOOH, CH_2Cl_2, 78%. [b]$(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78°C then olefination. [c]$Pd_2(dba)_3CHCl_3$, Ligand (**2a:** *n*-Bu_3P, **2b:** Ph_3P, **2c:** $(MeO)_3P$), HCO_2H, Et_3N, dioxane. [d]From **3b** to **1**, see ref. 3f); From **3c** to **1**, H_2, Pd/C, 83%.

Scheme 3

Results and Discussion

Epoxidation of (*E*)-2-methyl-2-penten-1-ol (**4**) using *t*-BuOOH in the presence of $Ti(O^iPr)_4$ and (+)-diethyl tartrate gave the chiral oxirane **5** in 91% yield. Swern oxidation of **5** followed by Wittig reaction with the phosphorane **6** gave the alkenyloxirane **2b** in 84 % yield from **5**. The alkenyloxirane **2b** was found to be stereochemically homogeneous by NMR. The vinylic proton of **2b** appears at δ 6.82, which shows the stereochemistry of the olefin is *E* form.[7] Reaction of the alkenyloxirane **2b** with formic acid in the presence of a catalytic amount of $Pd_2(dba)_3CHCl_3$ and PPh_3 gave the (*E*)-β,γ-unsaturated ester **3b** selectively in 75% yield and no formation of regio- and stereoisomer was observed. The formyl ester of **3b** is a known intermediate of (-)-serricornin.[3f]



6 **7** **8**

Scheme 4

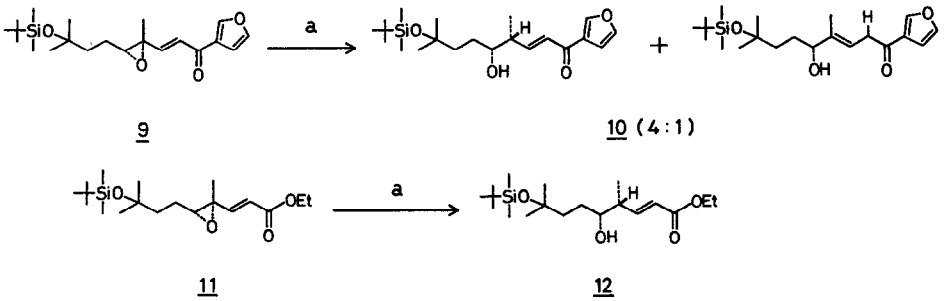
The (*E*)-alkenyloxirane **2c** was similarly obtained using the phosphorane **7** in 65% yield from **5**. Reaction of **2c** with formic acid using palladium-PPh_3 catalyst did not give satisfactory results compared with the hydrogenolysis of **2b** and the selectivity of conversion of **2c** was

examined using various phosphines or phosphites as ligands of the palladium catalyst. As shown in Table 1 the desired homoallylic alcohol **3c** was obtained as a major product in each case, but the undesired allylic alcohol **8**[8] was also formed in considerable yields. Among various ligands of palladium, trimethyl phosphite gave the most satisfactory result. The reaction of the alkenyloxirane **2c** with formic acid using palladium-$P(OMe)_3$ catalyst proceeded stereoselectively to give an 8:1 mixture of the α,β- and β,γ-unsaturated ketone, **3c** and **8**, in 48% yield and 50% of the unreacted oxirane was recovered.

Table 1: Regioselectivity of the hydrogenolysis of **2c** with formic acid using palladium-phosphine or phosphite ligand.

RUN	Palladium-catalyst	(Ligand/Pd = 0.5)	3c:8[a]	time(h)
1	$Pd_2(dba)_3CHCl_3$	none	2:1	2
2		Ph_3P	2:1	8
3		*n*-Bu_3P[b]	3:2	8
4		$(^iPrO)_3P$[c]	1:3	12
5		$(PhO)_3P$[d]	1:1	12
6		$(EtO)_3P$	4:1	8
7		$(MeO)_3P$	8:1-16:1	2
8		$(MeO)_3P$[e]	3:1	3
9		$(MeO)_3P$[ef]	17:2	3
10		$(MeO)_3P$ (L/Pd = 1)	4:1	2
11		$(MeO)_3P$ (L/Pd = 2)	4:1	2
12		$CH_3C(CH_2O)_3P$	4:1	3
13		$CH_3C(CH_2O)_3P$[e]	9:2	3
14	$(CH_3CO_2)_2Pd$	$(PhO)_3P$	N.R.	
15		Bu_3P	1:4	8

[a]GC analysis. [b]Reaction was carried out at 60°C. [c]Conversion of **2c** was 1%. [d]Conversion of **2c** was 75%. [e]Assay 98% of formic acid was used. [f]Water (1 equiv.) was added to the reaction mixture. [g]Conversion of **2c** was 18%.



9 **10** (4:1)

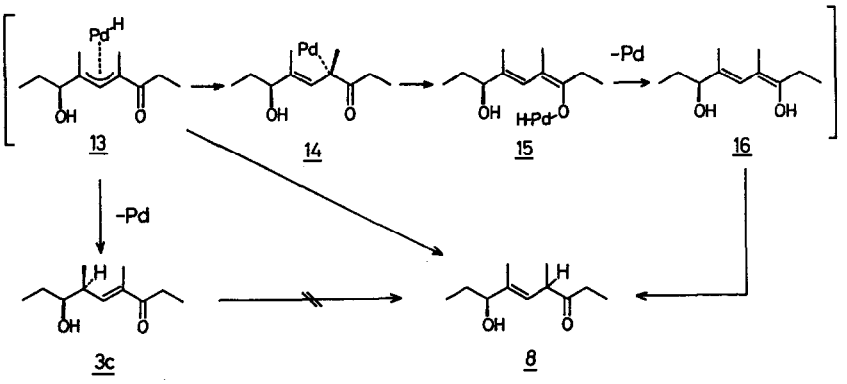
11 **12**

[a]$Pd_2(dba)_3CHCl_3$ (2.5 mol%), PPh_3 (2.5 mol%), HCO_2H (5 equiv.), Et_3N (2 equiv.), dioxane, r.t., 90-93%.

Scheme 5

The reaction of ester **2b** gave the homoallylic alcohol **3b** selectively without formation of a regio isomer. A similar loss of regioselectivity was observed in the reaction of **9** to **10**

which was an intermediate of nupharamine,[9] whereas the corresponding ester **11** was converted to α,β-unsaturated ester **12** selectively.[10] No isomerization of deconjugated ketone **8** to conjugated ketone **3c** was confirmed in the same reaction conditions. The difference of regioselectivity between esters and ketones is not clear but the formation of the β,γ-unsaturated ketone **8** is explained either by direct hydride attack to the π-allylpalladium complex **13** or by isomerization of **13** to the enolate complex **15** followed by reductive elimination and the subsequent isomerization of **16**.



Scheme 6

The unsaturated ketones **3c** and **8** can be separated by chromatography. Hydrogenation of the olefin of **3c** gave (-)-serricornin and its C-4 epimer with 1:1 ratio in 83% yield. The ratio of serricornin was raised to 3.9:1 by treatment of the mixture with *p*-toluenesulfonic acid in water and THF (1:1) at 50°C. Finally chromatographic purification gave the (-)-serricornin, which is identical with the one reported in the literature.[11] Optical purity of **3c** was found to be 88-96% determined by ^{1}H NMR of (*R*)-MTPA ester of **3c**.

Experimental Section.

General. Unless otherwise stated, experiments were carried out under argon atmosphere. Infrared spectra were obtained on a Shimadzu IR-400. ^{1}H NMR spectra were recorded on a JEOL GSX-400 in $CDCl_3$ or benzene-d_6 at 400 MHz, a Hitachi R-90H in $CDCl_3$ at 90 MHz, or a Hitachi R-24 in CCl_4 at 60 MHz. ^{13}C NMR spectra were recorded on a JEOL GSX-400 in $CDCl_3$ at 100.4 MHz or a Hitachi R-90H in $CDCl_3$ at 22.5 MHz. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Optical rotation was taken on a JASCO DIP-4. High resolution mass spectra were taken on a JEOL JMS-DX300. Ether, THF, and dioxane were distilled from benzophenone-ketyl. Benzene and dichloromethane (CH_2Cl_2) were distilled on diphosphorus pentaoxide. Dimethysulfoxide (DMSO) and triethylamine (Et_3N) were distilled on calcium hydride. Tri-*n*-butylphosphine (*n*-Bu_3P) was distilled in vacuo. Triphenylphosphine was recristalized from ethyl acetate. Tris(dibenzylideneacetone)-chloroform dipalladium ($Pd_2(dba)_3CHCl_3$) was prepared according to the literature.[12] Thin layer chromatography (TLC) was performed using Merck silica gel aluminum sheets (Art. 5554). Column chromatography was performed using Wakogel C-200 or Kanto silica gel 100-200 mesh.

(2S,3S)-Epoxy-2-methylpentan-1-ol (5). To a mixture of titanium tetraisopropoxide (892 μL, 3.0 mmol), L-(+)-diethyltartrate (513 μl, 3.0 mmol), and molecular sieves 4A in dry

CH_2Cl_2 (100 mL) was added the allylic alcohol **4** (3.00 g, 30.0 mmol) in CH_2Cl_2 (10 mL) with stirring at -23°C. To the mixture was added a solution of t-butyl hydroperoxide (4.2 M in $(CH_2Cl)_2$, 14.3 mL, 59.9 mmol) and the mixture was stirred for 2 h at -23°C. To the mixture was added Me_2S (4.4 mL, 60.0 mmol) at room temperature and the molecular sieves was filtered off. To the solution was added saturated aqueous NaF and the mixture was stirred for 24 h at room temperature. The mixture was passed through celite and the organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on SiO_2 column using a mixture of hexane–ethyl acetate (9:1) as an eluent to give **5** (3.15 g, 91% yield): $[\alpha]^{24.4}_D$ = -21.3° (*c* 1.78, $CHCl_3$); ^1H NMR (60 MHz, CCl_4) δ 3.24–3.64 (m, 2 H), 2.85 (d, *J* = 7.0 Hz, 1 H), 2.78 (d, *J* = 7.2 Hz, 1 H), 1.48 (dq, *J* = 6.0, 8.0 Hz, 2 H), 1.21 (s, 3 H), 1.02 (t, *J* = 6.0 Hz, 3 H); IR (neat) 3410, 2960, 1458, 1050, 930, 895, 835 cm^{-1}.

(1-Ethoxycarbonylethyl)-triphenylphosphonium bromide ($[Ph_3P^+CH(CH_3)CO_2Et]Br^-$). To a solution of triphenylphosphine (37.7 g, 144 mmoL) in benzene (300 mL) was added ethyl 2-bromopropanoate (25.9 g, 143 mmol) at room temperature and the mixture was stirred for 50 h. The white solid was separated by filtration and the cake was dried under reduced pressure to give (1-ethyoxycarbonylethyl)-triphenhylphosphonium bromide (31.0 g, 49% yield). The solid was used in the next step without purification.

Ethyl (*E*)-(4*S*,5*S*)-4,5-epoxy-2,4-dimethyl-2-heptenoate (2b). To a mixture of $(COCl)_2$ (7.21 mL, 82.6 mmol) in dry CH_2Cl_2 (70 ml) were added sequentially dry DMSO (12.2 mL, 172.2 mmol) and **5** (7.98 g, 68.7 mmol) in CH_2Cl_2 (10 ml) at -78°C and the mixture was stirred for 30 min. To the mixture was added Et_3N (48.0 mL, 144 mmol) and the mixture was stirred at room temperature for 1 h. To the mixture was added a solution of phosphorane **5** in THF which was prepared from $[Ph_3P^+CH(CH_3)CO_2Et]Br^-$ (36.6 g, 82.6 mmol) and *n*-BuLi (1.55 M in *n*-hexane, 44.4 mL, 68.8 mmol) in THF (100 mL) at 0°C. The solution was stirred for 2 h and *n*-hexane (200 mL) was added to the solution. The mixture was passed through celite and water was added to the solution. The organic layer was extracted with ether and the combined extracts were washed with $NaHCO_3$aq, NH_4Claq, and brine. The solution was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was chromatographed on SiO_2 using a mixture of ethyl acetate–hexane as an eluent to give **2b** (11.4 g, 84% yield); $[\alpha]^{23}_D$ = +78.3° (*c* 1.15, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 6.82 (d, *J* = 1.3 Hz, 1 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 2.81 (t, *J* = 6.2 Hz, 1 H), 1.92 (d, *J* = 1.4 Hz, 3 H), 1.61 (dq, *J* = 6.2, 7.8 Hz, 2 H), 1.39 (s, 3 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.8 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 166.7 (s), 134.0 (d), 128.9 (s), 64.2 (d), 60.0 (t), 58.2 (s), 21.4 (t), 16.3 (q), 13.6 (q), 12.6 (q), 9.8 (q); IR (neat) 2970, 1710, 1635, 1260 cm^{-1}; MS m/z 198, 180, 169, 165, 153, 139, 123, 112, 107, 95, 91, 79, 67, 61, 56, 53; HRMS calcd m/z 198.1256, found m/z 198.1280.

Ethyl (*E*)-(4*S*,5*S*)-5-hydroxy-2,4-dimethyl-2-heptenoate (3b). To a mixture of $Pd_2(dba)_2$-$CHCl_3$ (260 mg, 251 μmol) and PPh_3 (66.0 mg, 251 μmol) in dioxane (5 mL) was added a mixture of HCO_2H (2.31 g, 50.3 mmol) and Et_3N (2.80 mL, 20.1 mmoL) in dioxane (5 mL) at room temperature. The mixture was stirred for 5 min and **2b** (1.99 g, 10.1 mmoL) in dioxane (10 mL) was added to the solution. The mixture was stirred for 48 h and water (15 mL) was added to the solution. The organic layer was extracted with ether and the combined extracts were washed with NH_4Claq, $NaHCO_3$aq, and brine. The solution was dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on SiO_2 using a mixture of ether–hexane as an eluent to give **3b** (1.82 g, 90% yield): $[\alpha]^{26}_D$ = -25.0° (*c* 1.60, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 6.63 (dd, *J* = 1.4, 10.2 Hz, 1 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 3.53–3.22 (m, 1 H), 2.68–2.42 (m, 1 H), 1.86 (d, *J* = 1.4 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 144.5 (d), 127.9 (s), 76.1 (d), 60.9 (t), 39.8 (d), 28.2 (t), 15.8 (q), 14.7 (q), 13.1 (q), 10.6 (q); IR (neat) 3400, 2950, 1685, 1440, 1350, 1245, 1125, 930, 730 cm^{-1}; MS m/z 199, 186, 182, 169, 157, 153, 142, 129, 111, 95, 83, 69, 56, 53; HRMS calcd *m/z* 200.1413, found *m/z* 201.1253.

Preparation of 2-triphenylphosphranylidenepentan-3-one (7). To a mixture of water (72 mL) and acetic acid (48 mL) were added sequentially diethyl ketone (30 g, 345 mmol) and bromine (55.8 g, 155 mmoL) at 65–70°C. The mixture was stirred for 3 h and saturated aqueous sodium thiosulfate (100 mL) was added to the solution. The organic layer was extracted with CH_2Cl_2 and the combined extracts were washed with $NaHCO_3$aq, NH_4Claq, and brine. The

solution was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was distilled under reduced pressure (b.p. 80°C/25 mmHg) to give 2-bromopentan-3-one (25.7 g, 45% yield). ^1H NMR (60 MHz, CCl_4) δ 4.43 (q, J = 6.6 Hz, 1 H), 2.77 (q, J = 7.0 Hz, 1 H), 2.65 (q, J = 7.0 Hz, 1 H), 1.83 (d, J = 6.6 Hz, 3 H), 1.07 (t, J = 7.0 Hz, 3 H).

To a solution of triphenylphosphine (38.0 g, 145 mmoL) in benzene (80 mL) was added 2-bromopentan-3-one (25.7 g, 155 mmoL) at room temperature and the mixture was stirred for 3 d. The white solid was separated by filtration and the cake was dried under reduced pressure to give (3-oxo-2-pentyl)-triphenylphosphonium bromide (29.0 g, 47% yield). The solid was used in the next step without purification.

To a suspension of (3-oxo-2-pentyl)-triphenylphosphonium bromide (11.88 g, 30.0 mmol) in THF was added n-BuLi (1.6 M/L in hexane, 18.8 mL, 30.0 mmol) at 0°C and the mixture was stirred for 5 min. The solution containing the phosphorane **7** was used in the next reaction.

(E)-(6S,7S)-6,7-Epoxy-4,6-dimethyl-4-nonen-3-one (2c). By a similar procedure to **2b**, Swern oxidation of **5** (2.32 g, 20 mmol) followed by Wittig reaction with phosphorane **7** gave **2c** (2.32 g, 64% yield): $[\alpha]^{24}_D$ = 139° (c 2.12, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 6.69 (s, 1 H), 2.85 (t, J = 6.5 Hz, 1 H), 2.64 (q, J = 7.0 Hz, 2 H), 1.85 (s, 3 H), 1.42 (s, 3 H), 1.17-1.08 (m, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) 201.7 (s), 139.9 (s), 137.2 (d), 65.0 (d), 58.7 (s), 30.1 (t), 21.8 (t), 16.6 (q), 12.1 (q), 10.1 (q), 8.2 (q): IR (neat) 2975, 1680, 1460, 1380, 1220 cm^{-1}; MS: m/z 183, 165, 153, 137, 124, 109, 97, 91, 81, 67, 56, 53; HRMS calcd m/z 182.1307, found m/z 182.1302.

The palladium-catalyzed reaction of 2c with formic acid using various phosphine or phosphite ligand. According to the procedure for **3b** using various phosphine or phosphite as ligand (2.5 mol%) instead of PPh_3, hydrogenolysis of **2c** gave a mixture of **3c** and **8**. The ratio of the mixture and conversion of **2c** were estimated by GC analysis. **3c**: $[\alpha]^{23.6}_D$ = -34.7° (c 0.53, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 6.54 (dd, J = 10.0, 1.3 Hz, 1 H), 3.53-3.33 (m, 1 H), 2.70 (q, J = 7.5 Hz, 2 H), 2.76-2.65 (m, 3 H), 2.27 (s, 1 H), 1.81 (d, J = 1.4 Hz, 3 H), 1.20-0.90 (9 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 202.7 (s), 144.0 (d), 136.0 (s), 76.4 (d), 39.4 (d), 30.5 (t), 10.2 (q), 8.8 (q); IR (neat) 3400, 2950, 2925, 1710, 1660, 1460, 1380, 1045, 980, 735 cm^{-1}; MS m/z 185, 167, 155, 137, 126, 109, 97, 93, 81, 69, 58, 56, 53. The enantiomeric excess of **3c** was found to be 88-96% by NMR analysis of its (R)-MTPA ester.[13] **8**: ^1H NMR (90 MHz, $CDCl_3$) δ 5.31 (d, J = 9.1 Hz, 1 H), 3.86 (t, J = 6.6 Hz, 1 H), 3.42 (dq, J = 10.0, 6.5 Hz, 1 H), 2.57-2.30 (m, 2 H), 1.97 (b s, 1 H), 1.68 (t, J = 1.16 Hz, 3 H), 1.30-0.76 (13 H).

(*E*)-(6*S*,7*S*)-7-Hydroxy-4,6-dimethyl-4-nonen-3-one (3c). According to the procedure for **3b** using $(MeO)_3P$ (2.5 mol%), hydrogenolysis of **2c** gave a mixture of **3c** and **8** (51.0 mg, 48% yield), and recovered alkenyloxirane **2c** (37.7 mg, 35% yield).

(4*RS*,6*S*,7*S*)-7-Hydroxy-4,6-dimethyl-3-nonanone (a mixture of 1 and 4-epi-1). Hydrogen gas was bubbled through a mixture of (*E*)-(6*S*,7*S*)-4,6-dimethyl-7-hydroxy-4-penten-3-one (44.6 mg, 0.24 mmol) and Pd/C (5%, 51.4 mg, 24 μmol) in MeOH (4 mL) and the mixture was stirred for 24 h at room temperature. The solution was filtrated on celite and filtrate was concentrated to give the mixture of **1** and 4-epi-1 (1:1, 36.9 mg, 83% yield).

Epimerization of (4*R*,6*S*,7*S*)-7-Hydroxy-4,6-dimethyl-3-nonanone (4-epi-1) to (-)-sericornin (1). To a 1:1 mixture of **1** and 4-epi-1 (36.9 mg, 0.20 mmol) in THF (0.5 ml) and water (0.5 ml) was added a catalytic amount of p-TsOH and the mixture was stirred for 5 h at 50°C. The organic layer was extracted with ether and combined extracts were washed with brine. The solution was dried over $MgSO_4$ and concentrated in vacuo to give a 3.9:1 mixture of **1** and 4-epi-1 (30.6 mg, 83% yield). The mixture was chromatographed on SiO_2 column using a mixture of n-pentane-ether (95:5) as an eluent to give **1** (22.7 mg, 62% yield): $[\alpha]^{24}_D$ = -30.6° (c 1.08, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 3.10 (m, 1 H), 3.81 (ddd, J = 2.6, 5.9, and 8.1 Hz, 1 H). 13C NMR (100.3 MHz, C_6D_6) chain form: δ 7.4, 10.6, 11.7, 16.7, 26.1, 30.1, 31.2, 33.0, 36.1, 72.5, 98.5. Hemiacetal form: δ 8.0, 10.8, 13.7, 16.4, 27.5, 33.8, 35.8, 36.8, 43.7, 76.2, 213.5; IR (neat) 3475, 2963, 2934, 2878, 1710, 1463, 1379, 1273, 1146, 1099, 1039, 999, 962, 911 cm^{-1}.[14] Further elution with n-pentane-ether (7:3) gave (4*R*,6*S*,7*S*)-isomer (3.9 mg, 11%).

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