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CHEMOENZYMATIC SYNTHESIS OF FERRULACTONE II AND (2*E*)-9-HYDROXYDECENOIC ACID

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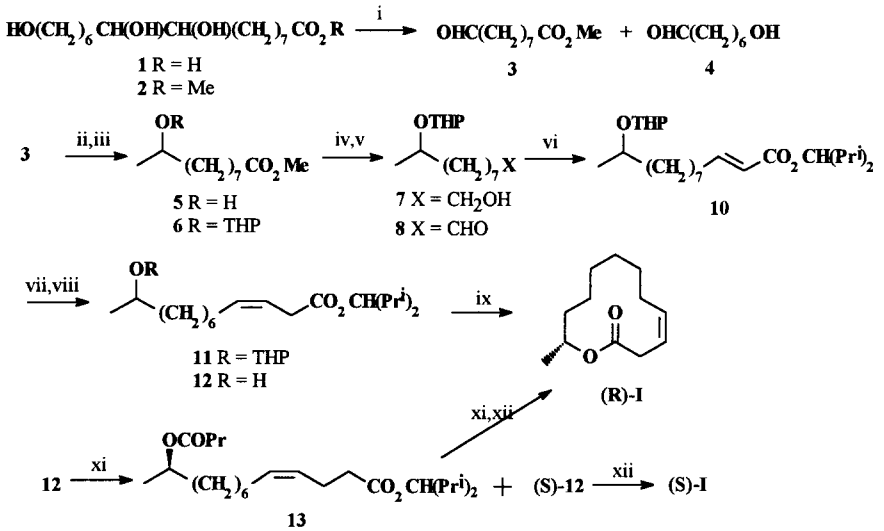
Abstract: A novel and divergent synthesis of the title compounds has been developed. The salient features of the synthesis were use of easily accessible starting material, regioselective organometallic reaction and enzymatic derivation of the key synthons.

(±)-Threo aleuritic acid **1**, easily accessible from shellac is extensively used by us in the synthesis of several achiral and chiral insect pheromones[1-3]. Its polyfunctionalities offer wide latitude in synthetic manoeuvers to render it a useful starting material. The α-glycol function present in **1** is especially attractive since its cleavage provides two bifunctional synthons which can be subsequently extended to different classes of bioactive compounds. Based on these, we have formulated a synthetic strategy for (3*Z*)-dodecen-12-olide **I** and (2*E*)-9-hydroxydecenoic acid (HDA) **II** in their antipodal forms. In this paper, we report the same. Compound **I**, commonly known as ferrulactone II is one of the major pheromone components of the male rusty grain beetle, *Cryptolestes ferrugineus*[4]. In addition, one of the notorious stored grain pests of global importance *viz.* *Cryptolestes pusilus*[5] also uses it as the pheromone. 9-HDA, on the other hand constitutes the mandibular gland secretion of queen bees, *Apis mellifera* L.[6,7] and helps in their retinue formation. The dependence of their bioactivities on the stereochemistry is intriguing. For instance, while (*S*)-**I** is the pheromone of both rusty and flat grain beetles, its enantiomer is the principal pheromone for the merchant grain beetles[8]. Likewise, (*R*)-HDA is ten fold more active than its antipode[9]. In view of all these, several chiral syntheses of **I**[10-12] and **II**[13,14] have appeared. However, the present brief and divergent synthesis for both of these from a single commercially available source seems a more practical approach.

Thus, the methyl ester **2**[15] of the acid **1** was subjected to $NaIO_4$ cleavage to furnish the C_9- and C_7-aldehyde derivatives **3** and **4**[3] respectively. The individual components could be separated efficiently by

evaporative distillation. Regioselective reaction of MeMgI with the aldehyde function of **3** was accomplished at -10° C in diethyl ether to afford the hydroxy ester **5**. After its pyranylation, the product **6** was reduced with LAH to give the diol derivative **7** which was subsequently oxidized to the aldehyde **8**. Its Wittig-Horner reaction with the bulky ylide **9**[16] furnished the conjugated ester **10**. This, on treatment with potassium hexamethyldisilazide resulted in the isomerization of its (2*E*)-olefin bond to the required (3*Z*)-compound **11**. Similar olefin migration-isomerization method has been used[16] by us recently for the synthesis of 1,4-dienic macrolide. After its depyranylation to the hydroxy ester **12**, we attempted its direct lactonization using lipase as the catalyst. Amongst the available lipases, only PPL could effect the transformation in benzene albeit in very poor yield (15%). Moreover, the undesired (*R*)-lactone was obtained with modest ee (65%). The absolute configuration was determined by comparing its sign of specific rotation with those reported[12]. The result was in accordance with one of its earlier synthesis[12] although the lipase used was different.



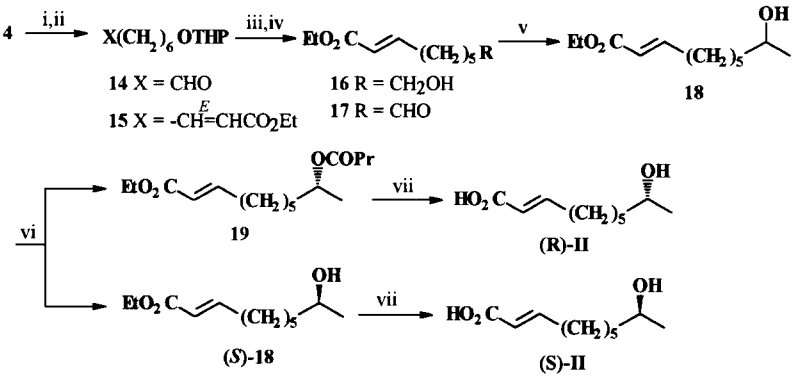
i) $NaIO_4$/MeCN/H_2O, ii) MeMgI/Et_2O/-10°C, iii) DHP/PPTS, iv) LAH/Et_2O, v) PCC/CH_2Cl_2, vi) NaH/$(EtO)_2P(O)CH_2CO_2CH(Pr^i)_2$ (**9**) /THF, vii) $KN(SiMe_3)_2$/THF/-78°C, viii) MeOH/PTS, ix) PPL/Benzene, x) TFEB/PPL/Cyclohexane, xi) alc. KOH, xii) Yamaguchi's method.

SCHEME 1

In view of the above, we attempted the resolution of **12** *via* its PPL catalyzed acylation with trifluoroethyl butyrate (TFEB). In cyclohexane, the (*R*)-butyrate **13** (68% ee) and (*S*)-**12** (91% ee) was obtained at ~50% conversion. A second acylation of the resolved alcohol (*S*)-**12** enriched its enantiomeric

excess to 98%. Compound (*S*)-**12** was then hydrolyzed with alc. KOH and subsequently lactonized following Yamaguchi's method[17] to furnish (*S*)-**I**.

For the synthesis of **II**, the aldehyde **4** was first pyranylated to compound **14** and then subjected to Wittig-Horner reaction with triethyl phosphonoacetate to give the ester **15** . After depyranylation, the product alcohol **16** was oxidized with PCC to afford the aldehyde **17** . As in the case of **3**, its reaction with MeLi at -40° C proceeded smoothly at the aldehyde site to produce the desired compound **18** . This was then resolved with PPL/TFEB in diisopropyl ether to get (*R*)-**19** (84% ee) and (*S*)-**18** (97% ee). The ee of **19** was improved to 95% by enzymatic alcoholysis with *n*-butanol using PPL as the catalyst. Alkaline hydrolysis of (*S*)-**18** and (*R*)-**19** finally led to (*S*)- and (*R*)-**II** respectively. In all the cases, the ees were determined by ^{1}H NMR analyses in presence of Eu(hfc)$_3$.



i) DHP/PPTS, ii) NaH/$(EtO)_2$P(O)CH_2CO_2Et/THF, iii) MeOH/PTS, iv) PCC/CH_2Cl_2, v) MeLi/Et_2O/-40°C, vi) TFEB/PPL/Diisopropyl ether, vii) alc. KOH.

SCHEME 2

EXPERIMENTAL

The IR spectra were scanned with a Perkin-Elmer spectrophotometer, model 783 and only the pertinent bands are mentioned. The PMR spectra were recorded with a Bruker AC-200 (200 MHz) instrument in $CDCl_3$. The optical rotaions were measured with a Jasco DIP-360 polarimeter. Anhydrous reactions were carried out under Ar using freshly distilled solvents.

Methyl 8-Formyloctanoate 3 and **7-Hydroxyheptanal 4** : To a cooled solution of **2** (15.0 g, 0.047 mol) in a mixture of CH_3CN-H_2O (3:2, 200 ml) was added $NaIO_4$ (12.8 g, 0.06 mol) in portions. The mixture was

stirred for 0.5 h and then filtered. The filtrate was extracted with $CHCl_3$, the extract washed with water and brine and dried. After concentration in vacuo the residue was distilled to furnish pure **3** and **4**[3].

3: yield: 6.7 g (76%); IR: 2740, 1750, 1720 cm^{-1}; PMR: δ 1.3 (s, 10H), 2.0-2.6 (m, 4H), 3.6 (s, 3H), 9.78 (t, J = 1.5 Hz, 1H).

Methyl 9-Hydroxydecanoate 5 : A solution of MeMgI [prepared from MeI (9.0 g, 0.063 mol) and Mg (1.85 g, 0.077 mol)] in ether (50 ml) was slowly added to a stirred and cooled (-10° C) solution of **3** (9.86 g, 0.053 mol) in ether (50 ml). After 1 h, the mixture was quenched with aq. sat. NH_4Cl solution, the oraganic layer separated and the aq. portion extracted with ether. The combined organic extract was washed with brine and dried. Solvent removal followed by column chromatography (silica gel, 0-20% EtOAc/hexane) of the residue gave pure **5**. yield: 8.7 g (81.3%); IR: 3400, 1750, 1450, 1200 cm^{-1}; PMR: δ 1.1 (d, J = 7 Hz, 3H), 1.28 (s, 12H), 2.1-2.4 (m, 2H), 2.8 (s, D_2O exchangeable, 1H), 3.5-3.8 (m containing a s at δ 3.54, 4H). Anal. Calcd. for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 65.12; H, 11.04.

Methyl 9-Tetrahydropyranyloxydecanoate 6 : A solution of **5** (4.0 g, 0.02 mol), DHP (2.0 g, 0.024 mol) and PPTS (0.1 g) in CH_2Cl_2 (60 ml) was stirred for 12 h at room temperature. It was quenched with aq. 10% $NaHCO_3$ solution, the organic layer separated and the aq. layer extracted with $CHCl_3$. The combined organic extract was washed with water and brine. After drying, it was concentrated in vacuo and the residue chromatographed over silica gel (0-5% EtOAc/hexane) to give **6**. yield: 5.15 g (91%); IR: 1760, 930, 880, 810 cm^{-1}; PMR: δ 1.1 (d, J = 7 Hz, 3H), 1.32 (s, 12H), 1.5-1.7 (m, 6H), 2.1-2.3 (m, 2H), 3.2-3.4 (m, 1.5H), 3.5-3.7 (m containing a s at δ 3.54, 4.5H), 4.12 (br. s, 0.5H), 4.53 (br. s, 0.5H). Anal. Calcd. for $C_{16}H_{30}O_4$: C, 67.09; H, 10.56. Found: C, 67.31; H 10.41.

9-Tetrahydropyranyloxydecan-1-ol 7 : To a stirred suspension of LAH (1.6 g, 0.042 mol) in ether (70 ml) was added **6** (10.0 g, 0.035 mol) in ether (30 ml). After refluxing for 4 h, the mixture was brought to room temperature and treated with aq. saturated Na_2SO_4 solution. The crystalline white solid was filtered off and the filtrate concentrated to furnish pure **7** after column chromatography (silica gel, 0-15% EtOAc/hexane). yield: 8.5 g (94.2%); IR: 3460, 1040, 930, 880, 810 cm^{-1}; PMR: δ 1.1 (d, J = 7 Hz, 3H), 1.3 (s, 14H), 1.4-1.7 (m, 6H), 2.42 (s, D_2O exchangeable, 1H), 3.3-3.5 (m, 2.5H), 3.7-4.0 (m, 2.5H), 4.5 (s, 0.5H), 4.9 (s, 0.5H). Anal. Calcd. for $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found: C, 69.57; H, 11.64.

9-Tetrahydropyranyloxydecan-1-al 8 : To a stirred suspension of PCC (5.0 g, 0.023 mol) and anhydrous NaOAc (0.66 g, 0.8 mmol) in CH_2Cl_2 (80 ml) was added the alcohol **7** (4.0 g, 0.016 mol) in one lot. Usual isolation provided the aldehyde **8** which was sufficiently pure (cf. TLC) and hence used as such for the next

step. yield: 3.56 g (89.8%); IR: 2720, 1710, 880, 810 cm^{-1}; PMR: δ 1.1 (d, J = 7 Hz, 3H), 1.3 (s, 12H), 1.4-1.6 (m, 6H), 2.21 (t, J = 7 Hz, 2H), 3.4-3.6 (m, 1.5H), 3.7-3.9 (m, 1.5H), 4.6 (s, 0.5H), 4.9 (s, 0.5H).

2',4'-Dimethyl-3"-pentyl (2*E*)-11-Tetrahydropyranyloxydodecenoate 10 : To a stirred and cooled (0° C) suspension of pentane-washed NaH (0.768 g, 0.016 mol, 50% suspension in oil) in THF (40 ml) was added the phosphonate **9** (4.7 g, 0.016 mol). After 0.5 h, the aldehyde **8** (3.5 g, 0.014 mol) in THF (10 ml) was added to it and the mixture stirred for 16 h at room temperature. The mixture was poured in ice-water, the THF layer separated and the aq. portion extracted with EtOAc. The organic extract was then washed with water and brine and finally dried. Removal of solvent followed by column chromatography over silica gel (0-10% EtOAc/hexane) afforded the ester **10**. yield: 3.93 g (71%); IR: 1720, 1660, 980, 910, 880 cm^{-1}; PMR: δ 0.88 (d, J = 6 Hz, 12H), 1.1 (d, J = 7 Hz, 3H), 1.3-1.6 (m, 12H), 1.7-1.9 (m, 8H), 2.1-2.4 (m, 2H), 3.3-3.5 (m, 1.5H), 3.6-3.9 (m, 1.5H), 4.52 (t, J = 7 Hz, 1H), 4.6 (s, 1H), 5.78 (d, J = 16 Hz, 1H), 6.88 (dt, J = 16 Hz, 5.4 Hz, 1H). Anal. Calcd. for $C_{24}H_{44}O_4$: C, 72.68; H, 11.18. Found: C, 72.54; H, 11.34.

2',4'-Dimethyl-3"-pentyl (3*Z*)-11-Tetrahydropyranyloxydodecenoate 11 : Following the reported[16] procedure, compound **10** (2.0 g, 0.005 mol) was isomerized with $KN(SiMe_3)_2$ [prepared from K (0.39 g, 0.01 mol), naphthalene (1.28 g, 0.01 mol) and HMDS (1.68 g, 0.01 mol)] in THF (30 ml) at -78° C. The product was purified by careful column chromatography over silica gel (0-10% ether/hexane). yield: 1.45 g (72.5%); IR: 1750, 1410, 1400, 910, 880 cm^{-1}; PMR: δ 0.9 (br. s, 12H), 1.1 (d, J = 7 Hz, 3H), 1.4-1.6 (m, 10H), 1.8-2.0 (m, 8H), 2.1-2.2 (m, 2H), 3.2 (d, J = 6 Hz, 2H), 3.6-3.9 (m, 3H), 4.6 (t, J = 7 Hz, 1H), 4.7 (s, 0.5H), 4.8 (s, 0.5H), 5.4-5.6 (m, 2H). Anal. Calcd. for $C_{24}H_{44}O_4$: C, 72.68; H, 11.18. Found: C, 72.44; H, 11.42.

2',4'-Dimethyl-3"-pentyl (3*Z*)-11-Hydroxydodecenoate 12 : A mixture of **11** (1.4 g, 3.5 mmol) and PTS (0.1 g) in MeOH (20 ml) was refluxed for 4 h. Most of the solvent was removed in vacuo, the residue taken in EtOAc and the solution washed with aq. 10% $NaHCO_3$, water and brine and dried. Removal of solvent followed by column chromatography (silica gel, 0-15% EtOAc/hexane) gave pure **12**. yield: 0.9 g (81.8%); IR: 3460, 3020, 1750, 1060 cm^{-1}; PMR: δ 0.9 (br. s, 12H), 1.1 (d, J = 7 Hz, 3H), 1.3-1.7 (m, 10H), 1.8-2.0 (m, 2H), 2.1-2.2 (m, 2H), 2.71 (s, D_2O exchangeable, 1H), 3.2 (d, J = 6 Hz, 2H), 3.6-3.9 (m, 1H), 4.6 (t, J = 7 Hz, 1H), 5.4-5.6 (m, 2H). Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61. Found: C, 72.88; H, 11.78.

(*R*)-Ferrulactone I : A mixture of **12** (0.5 g, 1.6 mmol) and PPL (0.5 g, Sigma. 53.2 units/mg) in benzene (50 ml) was stirred at room temperature for 72 h. After filtration, the solvent was removed and the product isolated by preparative TLC (silica gel, 20% EtOAc/hexane). yield: 0.047 g (15%); $[\alpha]^{22}$ -68.1 (c 0.7, $CHCl_3$) (lit[12]. $[\alpha]^{20}$ -82.29 (c 0.81, $CHCl_3$)); IR: 3020, 1725, 1660 cm^{-1}; PMR: δ 1.0 (d, J = 7 Hz, 3H), 1.3-1.7 (m, 10H),

2.0-2.4 (m, 2H), 2.9-3.1 (m, 2H), 4.5-4.6 (m, 1H), 5.3-5.6 (m, 2H). Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.31; H, 10.18.

(*R*)-2',4'-Dimethyl-3"-pentyl (3*Z*)-11-Butyroxydodecenoate 13 : A mixture of **12** (1.0 g, 3.2 mmol), TFEB (1.1 g, 6.4 mmol) and PPL (1.0 g, Sigma. 53.2 units/mg) in cyclohexane (20 ml) was stirred at room temperature. After 50% conversion, the enzyme was removed by filtration, the filtrate concentrated in vacuo and the residue purified by column chromatography (silica gel, 0-15% EtOAc/hexane).

13: yield: 0.585 g (48%); $[\alpha]^{22}$ -4.8 (c 0.7, $CHCl_3$); IR: 3020, 1750, 1260 cm^{-1}; PMR: δ 0.9 (s, 15H), 1.0 (d, J = 7 Hz, 3H), 1.3-1.7 (m, 12H), 1.8-2.0 (m, 2H), 2.1-2.2 (m, 2H), 2.5 (t, J = 6 Hz, 2H), 3.2 (d, J = 6 Hz, 2H), 4.1-4.3 (m, 1H), 4.6 (t, J = 7 Hz, 1H), 5.4-5.6 (m, 2H). Anal. Calcd. for $C_{23}H_{42}O_4$: C, 72.20; H, 11.07. Found: C, 72.12; H, 11.21.

12: yield: 0.437 g (43.7%); $[\alpha]^{22}$ +5.3 (c 1.22, $CHCl_3$). All other spectral data were identical with those of the racemic sample.

(*S*)-Ferrulactone I : A solution of (*S*)-**12** (0.45 g, 1.44 mmol) in alc. KOH (10 ml, 2N) was stirred at room temperature for 6 h. The mixture was concentrated in vacuo, EtOAc was added followed by dil. aq. HCl (2N) till acidic. The EtOAc extract was washed with water and brine. After drying, it was concentrated to give the corresponding acid. yield: 0.300 g (98%); $[\alpha]^{22}$ +6.45 (c 1.42, $CHCl_3$) (lit[12]. $[\alpha]^{22}$ +5.8 (c 0.52, $CHCl_3$)); IR: 3500-3200, 1710, 1060 cm^{-1}; PMR: δ 1.2 (d, J = 7 Hz, 3H), 1.34 (s, 10H), 1.9-2.2 (m, 2H), 3.12 (d, J = 5.4 Hz, 2H), 3.5-4.0 (m, 1H), 5.4-5.7 (m, 2H), 8.16 (s, D_2O exchangeable, 1H).

A mixture of above compound (39 mg, 0.18 mmol), TEA (34 ul) and 2,4,6-trichlorobenzoyl chloride (50 mg) in THF (15 ml) was stirred for 4 h at room temperature. The solution was filtered under Ar, the filtrate diluted to 100 ml with toluene and introduced into a refluxing solution of DMAP (150 mg) in toluene (20 ml) over a period of 3 h. After refluxing for an additional period of 3 h, it was brought to room temperature, washed with aq. 10% $NaHCO_3$, water and brine and dried. Solvent removal followed by preparative TLC gave pure (*S*)-**I**. yield: 21.8 mg (61%); $[\alpha]^{22}$ +82.3 (c 1.14, $CHCl_3$), (lit[12] $[\alpha]^{21}$ +73.9 (c 0.47, $CHCl_3$)). Its spectral data were identical with those of its antipode.

7-Tetrahydropyranyloxyheptanal 14 : Pyranylation of **4** (1.68 g, 0.013 mol) with DHP (1.2 g, 0.014 mol) in CH_2Cl_2 gave **14**. yield: 2.48 g (89.5%); IR: 2700, 1730, 910, 870, 810 cm^{-1}; PMR: δ 1.3-1.7 (m, 14H), 2.0-2.2 (m, 2H), 3.5-3.7 (m, 4H), 4.51 (s, 1H), 9.78 (t, J = 1.5 Hz, 1H).

Ethyl (2*E*)-9-Tetrahydropyranyloxynonenoate 15 : Wittig-Horner reaction between triethyl phosphonoacetate (2.84 g, 0.013 mol) and **14** (2.47 g, 0.012 mol) using NaH (0.672 g, 0.014 mol, 50%

suspension in oil) gave **15** after usual isolation. yield: 2.62 g (80%); IR: 1720, 1640, 980, 910, 870, 810 cm^{-1}; PMR: δ 1.2 (t, J = 7 Hz, 3H), 1.5 (br. s, 8H), 1.7 (br. s, 6H), 2.0-2.3 (m, 2H), 3.5-3.8 (m, 4H), 4.2 (q, J = 7 Hz, 2H), 4.51 (s, 1H), 5.88 (d, J = 16 Hz, 1H), 6.92 (dt, J = 16 Hz, 5.5 Hz, 1H). Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.42; H, 10.12.

Ethyl (2*E*)-9-Hydroxynonenoate 16 : Depyranylation of **15** (1.6 g, 5.6 mmol) with MeOH (10 ml) and PTS (0.1 g) gave the hydroxy ester **16**. yield: 0.81 g (72%); IR: 3360, 1730, 1640, 980 cm^{-1}; PMR: δ 1.2 (t, J = 7 Hz, 3H), 1.5 (br. s, 8H), 2.0-2.3 (m, 2H), 2.4 (s, D_2O exchangeable, 1H), 3.68 (t, J = 6 Hz, 2H), 4.14 (q, J = 7 Hz, 2H), 5.88 (d, J = 16 Hz, 1H), 6.92 (dt, J = 16 Hz, 5.5 Hz, 1H). Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.81; H, 10.22.

Ethyl (2*E*)-9-Formyloctenoate 17 : The above alcohol (0.528 g, 2.6 mmol) was oxidized with PCC (0.85 g, 3.9 mmol) in CH_2Cl_2 (30 ml) to furnish **17** after usual work-up. yield: 0.412 g (80%); IR: 2700, 1740, 1720, 1640, 980 cm^{-1}; PMR: δ 1.2 (t, J = 6 Hz, 3H), 1.4-1.7 (m, 6H), 1.9-2.3 (m, 4H), 4.1 (q, J = 7 Hz, 2H), 5.88 (d, J = 16 Hz, 1H), 6.92 (dt, J = 16 Hz, 5.5 Hz, 1H), 9.78 (t, J = 1.5 Hz, 1H).

Ethyl (2*E*)-9-Hydroxydecenoate 18 : To a stirred and cooled (-40° C) solution of **17** (1.0 g, 5.0 mmol) in ether (30 ml) was slowly added MeLi [prepared from Li (0.98 g, 14.0 mmol) and MeI (0.86 g, 6.0 mmol) in ether (20 ml)]. After 1 h, the mixture was treated with aq. saturated NH_4Cl, the ether layer separated and the aqueous portion extracted with EtOAc. The entire organic extract was washed with brine and dried. Solvent removal in vacuo followed by column chromatography (silca gel, 0-15% EtOAc) of the residue gave pure **18**. yield: 0.734 g (68%); IR: 3360, 1740, 1640, 980 cm^{-1}; PMR: δ 1.1-1.3 (m, 6H), 1.5 (br. s, 8H), 1.8 (s, D_2O exchangeable, 1H), 2.2-2.4 (m, 2H), 3.7-3.9 (m, 1H), 4.2 (q, J = 7 Hz, 2H), 5.88 (d, J = 6 Hz, 1H), 6.92 (dt, J = 16 Hz, 5.5 Hz, 1H). Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.18; H, 10.14.

Ethyl (9*R*,2*E*)-9-Butyroxydecanoate 19 : A mixture of compound **18** (0.7 g, 3.3 mmol), TFEB (1.11 g, 6.6 mmol) and PPL (1.0 g) in diisopropyl ether (20 ml) was stirred for 48 h. The reaction products were isolated in pure forms as was done for compound **12**.

19: yield: 0.440 g (47.4%); $[\alpha]^{22}$ -4.1 (c 1.88, $CHCl_3$); IR: 1740, 1640, 980 cm^{-1}; PMR: δ 0.9 (dist. t, 3H), 1.2-1.3 (m, 6H), 1.4 (br. s, 10H), 2.1-2.3 (m, 2H), 2.48 (t, J = 6 Hz, 2H), 3.7-3.9 (m, 1H), 4.2 (q, J = 7 Hz, 2H), 5.88 (d, J = 16 Hz, 1H), 6.92 (dt, J = 16 Hz, 5.5 Hz, 1H). Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.48; H, 9.78.

18: yield: 0.298 g (42.6%); $[\alpha]^{22}$ +6.1 (c 2.02, $CHCl_3$). All other spectral data were identical with those of the racemic sample.

(9*R*,2*E*)-9-Hydroxydecenoic acid II : Alkaline hydrolysis of **19** (0.284 g, 1.0 mmol) gave (*R*)-**II** after usual isolation. yield: 0.163 g (88%); $[\alpha]^{22}$ -8.3 (c 2.19, CH_3OH), (lit[13]. $[\alpha]^{20.5}$ -7.95 (c 16.48, CH_3OH)); IR: 3700 -3440, 1710, 1640, 980 cm^{-1}; PMR: δ 1.12 (d, J = 6 Hz, 3H), 1.32 (br. s, 8H), 2.1-2.2 (m, 2H), 2.44 (s, D_2O exchangeable, 1H), 3.7-3.9 (m, 1H), 5.88 (d, J = 16 Hz, 1H), 6.92 (dt, J = 16 Hz, 5.5 Hz, 1H), 8.01 (s, D_2O exchangeable, 1H). Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H 9.74. Found: C, 69.27; H, 9.96.

(9*S*,2*E*)-9-Hydroxydecenoic acid II : Compound (*S*)-II was prepared as above, which showed identical spectral properties. $[\alpha]^{22}$ -8.5 (c 1.47, CH_3OH), (lit[13]. $[\alpha]^{20.5}$ +8.51 (c 12.92, CH_3OH)).

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