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# Enantiomeric synthesis of the key synthon of the oviposition-deterring pheromone of *Rhagoletis cerasi* L.

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***Abstract:*** A convenient and enantioselective synthesis of ethyl (8*RS*,15*R*)-8-acetoxy-15-hydroxyhexadecanoate **15** via a chemoenzymatic approach has been described. The salient features of the synthesis were operational simplicity, use of easily accessible materials, and excellent enantiocontrol via lipase catalyzed acetylation of 2-alkanol. © 1997 Elsevier Science Ltd. All rights reserved.

Development of reliable plant protection measures is crucial for progress in the productivity of modern agricultural systems. Programs such as IPM demonstrate the utility and application of pheromones to reduce the infestation of crops by pests in an eco-friendly manner. The oviposition-deterring pheromone (ODP)[1] of the European cherry fruit fly, *Rhagoletis cerasi* L., which has been identified as the ammonium salt of 2-{[15-[β-D-glucopyranosyl)oxy]-8-hydroxyhexadecanoyl]amino}ethanesulfonic acid **I** constitutes one such compound of economic significance. The primary role of the pheromone is to mark the fruits already used for egg laying by the insect.

It stands out as a rare example of a glycoside, showing pheromonal activity. Isolation of **I** as an insect pheromone is rather surprising considering that pheromone perception is fundamentally olfactory in nature, although gustatory perception is also known. Thus, it is no wonder that the majority of insect pheromones are volatile compounds, more so for the defense and aggregation substances. Despite having two stereogenic centres, the natural compound is known to possess (*R*)-configuration at C-15 and is a 1:1 mixture of epimers at C-8.[2] So far, three syntheses[3–5] of **I** and the corresponding sodium salt have been reported in literature. Most of these suffer from circuitous routes, poor yield and/or use of difficult-to-access starting materials.

Considering the above limitations of the earlier syntheses for **I** or its other derivatives, the need to develop a short and efficient synthesis was apparent. For this, we envisaged that the use of enzymatic reactions would not only ensure excellent enantiocontrol but also provide a shorter route to the target compound. Consequently, we attempted to prepare ethyl (8*RS*,15*R*)-15-hydroxy-8-acetoxyhexadecanoate **15**, the immediate progenitor of the target pheromone. Since the stereochemistry at its C-8 centre is of no consequence to the biological activity, we restricted (Scheme 1) our attention to the stereochemistry at the C-15 centre only. The synthon **15** can be easily elaborated to the pheromone **I** by glycosylation[6] and subsequent formation of taurin amide.[7]

Thus, 1,8-octanediol **1** was monosilylated to give compound **2** which on oxidation with 'buffered PCC' furnished the aldehyde **3**. Its reaction with methylmagnesium iodide afforded the hydroxy compound **4** in excellent yield. At this stage, it was necessary to introduce the asymmetry required for the target compound. Earlier, we and others developed[8a,b] efficient lipase catalyzed acylation strategies for the resolution of 2-alkanols and their derivatives. In the present synthesis a similar strategy was attempted for the resolution of **4**. Thus, compound **4** was subjected to porcine pancreatic lipase (PPL) catalyzed acylation under different conditions viz. different acylating agents and solvents, and extent of conversion (Table 1).

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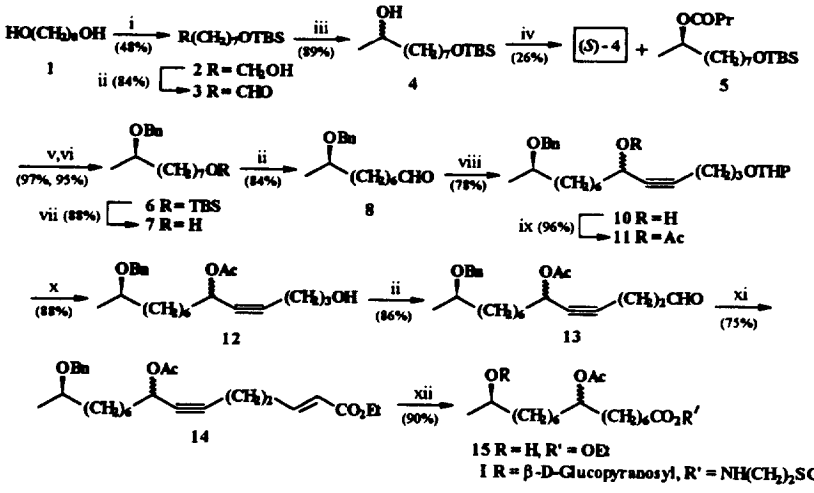

i) TBSCl/TEA/DMAP/$CH_2Cl_2$, ii) PCC/NaOAc/$CH_2Cl_2$, iii) MeI/Mg/ether, iv) PPL/TFEB/Diisopropyl ether, v) Alcoholic KOH, vi) BnBr/NaH, vii) TBAF/THF, viii) *n*-BuLi/THF/HC≡C$(CH_2)_3$OTHP (9), ix) $Ac_2O$/Pyridine, x) LiCl/DMSO/$H_2O$/Δ, xi) NaH/THF/$(EtO)_2P(O)CH_2CO_2Et$, xii) $H_2$/10% Pd-C/EtOH.

**Scheme 1.**

**Table 1.** Effect of reaction parameters on PPL catalysed resolution of **4**

| Acylating agent | Solvent | Conversion | % ee of ester (config.) | % ee of alcohol |
|---|---|---|---|---|
| Vinyl acetate | Hexane | 17 | 78 (*R*) | 48 |
| Vinyl acetate | Diisopropyl ether | 26 | 77 (*R*) | 61 |
| TFEB | Hexane | 14 | 92 (*R*) | 65 |
| TFEB | Diisopropyl ether | 30 | 93 (*R*) | 78 |

The best result was obtained with trifluoroethyl butyrate (TFEB) as the acyl donor in diisopropyl ether when at 30% conversion, the (*R*)-butyrate **5** and (*S*)-**4** were obtained with 93% and 78% ees respectively. A second acylation of the above alcohol led to its enantiomeric enrichment to 92% after ~35% conversion. The % ee of the alcohol **4** was assayed by the GLC analysis of its (*R*)-MTPA ester. The % ee of the butyrate **5** was likewise determined after converting it to the alcohol (*R*)-**4**. The configurational assignments were inferred from the general trend[8] of PPL catalyzed acylation of 2-alkanols and their derivatives. For further confirmation, (*R*)-**4** was converted to the known[9] compound (*R*)-2-nonanol via pyranylation, desilylation, mesylation, LAH reduction and depyranylation. Comparison of the sign of its specific rotation with that reported confirmed the above assignment.

For the synthesis of **15**, the ester (*R*)-**5** was hydrolyzed with alcoholic KOH and the hydroxyl function of the resultant compound (*R*)-**4** benzylated to furnish **6**. Its desilylation gave the hydroxy compound **7** which on PCC oxidation gave the aldehyde **8**. This was then reacted with the C-lithio derivative of the known compound **9**[10] to afford **10**. After its acetylation to **11**, the compound was subjected to acid catalyzed depyranylation. However, this led to a mixture of depyranylated and deacetylated products in almost equal amounts. Consequently, the desired depyranylation was carried out in excellent yield by heating it with LiCl in aqueous DMSO following a recently reported method.[11] The resultant compound **12** was oxidized to the aldehyde **13** and subjected to Wittig–Horner olefination with triethyl phosphonoacetate to furnish the conjugated ester **14**. Finally, catalytic hydrogenation of **14** over 10% Pd–C furnished the target hydroxy ester **15** with concomitant debenzylation.

## Experimental

All the boiling points are uncorrected. The IR spectra were scanned as thin films with a Perkin–Elmer spectrophotometer model 837. The $^1H$ NMR spectra were recorded in $CDCl_3$ with a Bruker AC-200 (200 MHz) instrument. The optical rotations were measured with a Jasco DIP 360 polarimeter. The GLC analyses were carried out using a Shimadzu GC-7A chromatograph fitted with a stainless steel column and flame ionization detector using 3% OV-17 (2 m×0.5 mm) column and a $N_2$ flow rate 40 mL/min. Anhydrous reactions were carried out under Ar using freshly dried solvents. The organic extracts were dried over anhydrous $Na_2SO_4$. For enzymatic resolution PPL (Sigma, sp. act. 52.4 units/mg) was used as obtained. Solvents for enzymatic reactions viz. diisopropyl ether, toluene, hexane, dichloromethane, THF (E. Merck, AnalR) were desiccated over freshly activated 4 Å molecular sieve (Linde) at 25°C for 72 h prior to use.

*8*-tert-*Butyldimethylsilyloxyoctan-1-ol* **2**

A mixture of 1,8-octanediol (10.0 g, 0.068 mol), triethylamine (7.60 g, 0.075 mol), 4,4′-dimethylaminopyridine (DMAP) (0.334 g, 2.73 mmol) and *tert*-butyldimethylsilyl chloride (TBSCl) (11.38 g, 0.075 mol) in $CH_2Cl_2$ (75 ml) was stirred till the appearance of disilylated product (*cf.* TLC, ~6 h). The mixture was poured into ice cold water, the organic layer separated and the aqueous portion extracted with $CHCl_3$. The combined organic extract was washed with aqueous HCl (2 N), water and brine. After drying and concentration of the extract in vacuo, the residue obtained was purified by column chromatography (silica gel, 0–15% EtOAc:hexane) to give **2**. Yield: 8.5 g (48%); IR: 3340, 1470, 1260, 1090 $cm^{-1}$; PMR: δ 0.12 (s, 6H), 0.88 (s, 9H), 1.1–1.6 (m, 12H), 2.9 (s, $D_2O$ exchangeable, 1H), 3.5–3.7 (m, 4H). Anal. Calcd for $C_{14}H_{32}O_2Si$: C 64.55, H 12.38. Found: C 64.79, H 12.16.

*8*-tert-*Butyldimethylsilyloxyoctanal* **3**

To a stirred suspension of pyridinium chlorochromate (PCC) (3.23 g, 0.015 mol) in $CH_2Cl_2$ (30 ml) and NaOAc (0.082 g, 0.001 mol) was added compound **2** (2.60 g, 0.01 mol) in (10 ml). After ~3 h, the mixture was diluted with solvent ether (50 ml) and the supernatant passed through a 2 in. pad of silica gel. The eluent was concentrated under vacuum to furnish **3** which was sufficiently pure and hence used as such in the next step. Yield: 2.16 g (84%); IR: 2720, 1720, 1470, 1260 $cm^{-1}$; PMR: δ 0.12 (s, 6H), 0.88 (s, 9H), 1.2–1.6 (m, 10H), 2.1–2.3 (m, 2H), 3.61 (t, *J*=6 Hz, 2H), 9.8 (t, *J*=1.5 Hz, 1H).

*1*-tert-*Butyldimethylsilyloxynonan-8-ol* **4**

To a stirred solution of methylmagnesium iodide [prepared from MeI (2.41 g, 0.017 mol) and Mg (0.485 g, 0.02 mol)] in anhydrous ether (30 ml)] was added **3** (2.16 g, 8.37 mmol) in ether (15 ml) at 0°C. After 3 h, the reaction was quenched with aqueous saturated $NH_4Cl$ and the mixture extracted with ether. The ether layer was washed with water and brine and dried. Removal of solvent under reduced pressure followed by column chromatography of the residue over silica gel (0–20% EtOAc:hexane) gave pure **4**. Yield: 2.04 g (89%); IR: 3360, 1465, 1100 $cm^{-1}$; PMR: δ 0.12 (s, 6H), 0.9 (s, 9H), 1.18 (d, *J*=6 Hz, 3H), 1.3–1.7 (m, 12H), 2.36 (s, $D_2O$ exchangeable, 1H), 3.63 (t, *J*=6 Hz, 2H), 3.7–3.9 (m, 1H). Anal. Calcd for $C_{15}H_{34}O_2Si$: C 65.63, H 12.48. Found: C 65.48, H 12.31.

*(8R)-1*-tert-*Butyldimethylsilyloxy-8-butyroxynonane* **5**

A mixture of (±)-**4** (2.0 g, 7.29 mmol), TFEB (1.85 g, 10.9 mmol) and PPL (0.5 g) in diisopropyl ether (40 ml) was magnetically stirred. After 18 h, at 30% conversion (*cf.* GLC), the reaction mixture was filtered and the residue chromatographed (silica gel, 0–20% EtOAc:hexane) to obtain pure (*R*)-**5**. Yield: 0.652 g (26%); $[\alpha]_D^{24}$ +14.18 (c 1.4, $CHCl_3$); IR: 1740, 1230, 880, 810 $cm^{-1}$; PMR: δ 0.12 (s, 6H), 0.9 (s, 12H), 1.2 (d, *J*=6 Hz, 3H), 1.3–1.6 (m, 14H), 2.3 (t, *J*=6 Hz, 2H), 3.68 (t, *J*=6 Hz, 2H), 4.0–4.3 (m, 1H). Anal. Calcd for $C_{19}H_{40}O_3Si$: C 66.22, H 11.70. Found: C 66.08, H 11.61. (*S*)-**4**: yield: 1.26 g (63%); $[\alpha]_D^{24}$ −9.36 (c 0.7, $CHCl_3$).

*(8S)*-tert-*Butyldimethylsilyloxynonan-8-ol* ***4***

Esterification of the above (*S*)-**4** (1.26 g, 4.6 mmol), TFEB (1.17 g, 6.9 mmol) and PPL (0.35 g) in diisopropyl ether (30 ml) was carried out as described previously to obtain optically enriched (*S*)-**4**. Yield: 0.718 g (57%); $[\alpha]_D^{24}$ −10.88 (c 2.1, $CHCl_3$).

*(8R)-1-*tert-*Butyldimethylsilyloxynonan-8-ol* ***4***

A solution of **5** (0.650 g, 1.89 mmol) in alcoholic KOH (10 ml, 2 N) was stirred at room temperature until completion of the reaction (*cf.* TLC, ~12 h). Most of the solvent was removed in vacuo and the residue extracted with ether. The ether layer was washed with water and brine and finally dried. Solvent removal followed by column chromatography (silica gel, 0–15% EtOAc/hexane) of the residue gave pure (*R*)-**4** whose spectral properties were identical with those of the racemic sample. Yield: 0.5 g (97%); $[\alpha]_D^{24}$ +11.1 (c 0.8, $CHCl_3$).

*MTPA ester of* ***4***

To a solution of **4** (10 mg) in anhydrous pyridine (0.5 ml) were added four mole excess of α-methoxy-α-trifluoromethylphenylacetic acid chloride and 1–2 crystals of 4-dimethylaminopyridine. The mixture was stirred overnight at room temperature, most of the solvent removed in vacuo and the residue subjected to preparative TLC (silica gel, 10% EtOAc:hexane) to isolate the respective MTPA esters which were analyzed by GLC (3% OV-17 column, temperature programming 140–240°C, 4°C/min, $t_R$=18.6 min and 19.2 min for (*R*)-**4** and (*S*)-**4** respectively.

*(8R)-1-*tert-*Butyldimethylsilyloxy-8-benzyloxynonane* ***6***

To a stirred suspension of hexane-washed NaH (0.138 g, 2.88 mmol, 50% dispersion in oil) in THF (20 ml) was added (*R*)-**4** (0.718 g, 2.62 mmol) in THF (10 ml). After the addition, the mixture was heated to 60°C for 1 h. It was cooled to room temperature, BnBr (0.896 g, 5.24 mmol) in THF (10 ml) was introduced into it and stirring continued overnight. On completion of the reaction, the mixture was poured into cold water and extracted with ether. The ether extract was washed with water and brine and dried. Purification of the residue by column chromatography over silica gel (0–10% EtOAc:hexane) gave pure **6**. Yield: 0.905 g (95%); $[\alpha]_D^{22}$ +12.6 (c 0.68, $CHCl_3$); IR: 3065, 3030, 1570, 1100, 700 $cm^{-1}$; PMR: δ 0.12 (s, 6H), 0.9 (s, 9H), 1.16 (d, *J*=6 Hz, 3H), 1.32 (m, 12H), 4.5 (s, 2H), 3.6–3.9 (m, 3H), 7.16 (br. s, 5H). Anal. Calcd for $C_{22}H_{40}O_2Si$: C 72.47, H 11.06. Found: C 72.68, H 10.86.

*(8R)-8-Benzyloxynonan-1-ol* ***7***

To a cooled (−78°C) and stirred solution of **6** (0.900 g, 2.47 mmol) in THF (10 ml) was added $Bu_4NF$ (2.7 ml, 2.7 mmol, 1.0 M solution in THF) and stirring continued until the reaction was complete (*cf.* TLC). The mixture was poured into ice cold water and extracted with solvent ether. The extract was washed with water and brine and finally dried. Removal of solvent followed by column chromatography of the residue (silica gel, 0–15% EtOAc:hexane) furnished **7**. Yield: 0.543 g (88%); $[\alpha]_D^{22}$ +8.0 (c 1.12, $CHCl_3$); IR: 3380, 3065, 3030, 700 $cm^{-1}$; PMR: δ 1.18 (d, *J*=6 Hz, 3H), 1.2–1.5 (m, 12H), 2.4 (s, $D_2O$ exchangeable, 1H), 3.68 (t, *J*=6 Hz, 2H), 4.0–4.2 (m, 1H), 4.5 (s, 2H), 7.16 (br. s, 5H). Anal. Calcd for $C_{16}H_{26}O_2$: C 76.75, H 10.47. Found: C 76.60, H 10.71.

*(8R)-8-Benzyloxynonanal* ***8***

As described for the preparation of **3**, compound **7** (0.543 g, 2.17 mmol) was oxidized with PCC (0.700 g, 3.26 mmol) in $CH_2Cl_2$ (20 ml) to give **8**. Yield: 0.452 g (84%); IR: 3090, 3065, 3030, 2720, 1725 $cm^{-1}$; PMR: δ 1.16 (d, *J*=7 Hz, 3H), 1.2–1.5 (m, 10H), 2.2–2.4 (m, 2H), 3.7–3.9 (m, 1H), 4.5 (s, 2H), 7.21 (br. s, 5H), 9.8 (t, *J*=1.5 Hz, 1H).

*(6RS,13R)-6-Hydroxy-13-benzyloxy-1-tetrahydropyranyloxytetradec-4-yne* ***10***

To a stirred suspension of **9** (0.368 g, 2.19 mmol) in THF (20 ml) at −25°C was added *n*-BuLi (1.37 ml, 1.6 M in hexane, 2.19 mmol). After stirring for 1 h at the same temperature, it was cooled to −30°C

and the aldehyde **8** (0.452 g, 1.82 mmol) in THF (10 ml) was added. The mixture was stirred for 4 h at −30°C and 12 h at room temperature. It was treated with aqueous saturated $NH_4Cl$, the organic part separated and the aqueous portion extracted with ether. The combined organic extract was washed with water and brine and finally dried. Removal of solvent and subsequent column chromatography of the product over silica gel (0–20% EtOAc:hexane) gave pure **10**. Yield: 0.59 g (78%); $[\alpha]_D^{22}$ +4.41 (c 0.86, $CHCl_3$); IR: 3420, 3080, 3065, 2235, 870, 810 $cm^{-1}$; PMR: δ 1.14 (d, *J*=7 Hz, 3H), 1.32 (br. s, 14H), 1.5–1.7 (m, 6H), 2.1–2.3 (m, 2H), 2.7 (br. s, $D_2O$ exchangeable, 1H), 3.6–4.2 (m, 5H), 4.3–4.4 (m, 1H), 4.5 (s, 1H), 4.55–4.6 (br. s, 2H), 7.16 (br. s, 5H). Anal. Calcd for $C_{26}H_{40}O_4$: C 74.96, H 9.68. Found: C 75.14, H 9.78.

*(6*RS,*13*R*)-6-Acetoxy-13-benzyloxy-1-tetrahydropyranyloxytetradec-4-yne* ***11***

A mixture of **10** (0.590 g, 1.42 mmol) and $Ac_2O$ (1.0 ml) in pyridine (1.0 ml) was stirred for 12 h. Ice cold water was added to the mixture and stirring continued for an additional 2 h. The mixture was extracted with solvent ether, the extract washed with water and brine and dried. After concentration in vacuo, the residue was chromatographed over silica gel (0–10% ether:hexane) to furnish **11**. Yield: 0.624 g (96%); $[\alpha]_D^{22}$ +7.0 (c 0.52, $CHCl_3$); IR: 3020, 2245, 1740, 1240, 880, 820 $cm^{-1}$; PMR: δ 1.14 (d, *J*=7 Hz, 3H), 1.3 (br. s, 14H), 1.5–1.7 (m, 6H), 2.18 (t, *J*=6 Hz, 2H), 2.26 (s, 3H), 3.5–4.3 (m, 5H), 4.5–4.7 (m, 4H), 7.35 (s, 5H). Anal. Calcd for $C_{28}H_{42}O_5$: C 73.33, H 9.23. Found: C 73.57, H 9.38.

*(6*RS,*13*R*)-6-Acetoxy-13-benzyloxytetradec-4-yn-1-ol* ***12***

A mixture of **11** (0.624 g, 1.36 mmol), LiCl (0.293 g, 6.9 mmol) and water (0.25 ml, 14.0 mmol) in DMSO (10 ml) was heated for 16 h at 90°C, at which time no starting material was noticed in the TLC. The mixture was brought to room temperature, poured into a large excess of water and extracted with EtOAc. The organic extract was washed with water and brine, dried and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 0–15% EtOAc:hexane) to furnish **12**. Yield: 0.447 g (88%); $[\alpha]_D^{22}$ +4.57 (c 0.76, $CHCl_3$); IR: 3400, 3060, 1580, 1460, 1240 $cm^{-1}$; PMR: δ 1.14 (d, *J*=7 Hz, 3H), 1.2–1.4 (m containing a s at 1.29, 14H), 2.18 (t, *J*=7 Hz, 2H), 2.21 (s, 3H), 2.8 (br. s, $D_2O$ exchangeable, 1H), 3.68 (t, *J*=6 Hz, 2H), 3.9–4.0 (m, 1H), 4.2–4.7 (m, 3H), 7.3 (s, 5H). Anal. Calcd for $C_{23}H_{34}O_4$: C 73.76, H 9.15. Found: C 73.57, H 9.27.

*(6*RS,*13*R*)-6-Acetoxy-13-benzyloxytetradec-4-ynal* ***13***

As described for the preparation of **3**, compound **12** (0.441 g, 1.18 mmol) was oxidized with PCC (0.380 g, 1.76 mmol) and NaOAc (50 mg) in $CH_2Cl_2$ (15 ml) to give **13**. Yield: 0.377 g (86%); IR: 2720, 1720, 1580, 1400 $cm^{-1}$; PMR: δ 1.16 (d, *J*=7 Hz, 3H), 1.3 (br. s, 12H), 2.19 (s, 3H), 2.3–2.5 (m, 4H), 3.7–3.9 (m, 1H), 4.2–4.6 (m, 3H), 7.3 (s, 5H), 9.78 (t, *J*=1.5 Hz, 1H).

*Ethyl (2*E,*8*RS,*15*R*)-8-Acetoxy-15-benzyloxyhexadec-2-en-6-ynoate* ***14***

To a stirred suspension of NaH (0.058 g, 1.2 mmol, 50% dispersion in oil) in THF (20 ml) was added triethyl phosphonoacetate (0.272 g, 1.2 mmol) in THF (10 ml). After stirring for 0.5 h, the resulting clear solution was cooled to 0°C and compound **13** (0.377 g, 1.01 mmol) in THF (10 ml) added in dropwise fashion. Stirring was continued for 3 h at the same temperature and for 15 h at room temperature. The mixture was poured into water, the organic layer separated and the aqueous portion extracted with ether. The combined organic extract was washed with water and brine, dried and concentrated in vacuo. The crude product was purified by column chromatography (0–10% EtOAc:hexane) to furnish **14**. Yield: 0.336 g (75%); $[\alpha]_D^{22}$ +7.28 (c 0.52, $CHCl_3$); IR: 2250, 1720, 1650, 980 $cm^{-1}$; PMR: δ 1.14 (overlapped d and t, 6H), 1.29 (br. s, 12H), 2.14 (s, 3H), 2.2–2.5 (m, 4H), 3.7–4.6 (m containing a q at δ 4.12, 6H), 5.78 (d, *J*=16 Hz, 1H), 6.7–6.9 (m, 1H), 7.3 (s, 5H). Anal. Calcd for $C_{27}H_{38}O_5$: C 73.27, H 8.65. Found: C 73.12, H 8.48.

*Ethyl (8*RS,*15*R*)-8-Acetoxy-15-hydroxyhexadecanoate* ***15***

A mixture of **14** (0.336 g, 0.76 mmol) and 10% Pd–C (30 mg) in EtOH (10 ml) was magnetically stirred under a slight positive pressure of $H_2$ gas. After the required uptake of the gas, the mixture was

diluted with ether and passed through a 2 in. pad of silica gel. The eluent was concentrated in vacuo and the residue purified by column chromatography (silica gel, 0–10% EtOAc:hexane) to furnish pure **15**. Yield: 0.244 g (90%); $[\alpha]_D^{22}$ +6.2 (c 0.9, $CHCl_3$); IR: 3420, 1740, 1100, 1040 $cm^{-1}$; PMR: δ 1.1 (overlapped d and t, 6H), 1.3 (br. s, 22H), 2.12 (s, 3H), 2.32 (t, *J*=7 Hz, 2H), 2.41 (br. s, $D_2O$ exchangeable, 1H), 3.7–3.8 (m, 1H), 4.1–4.4 (m containing a q at δ 4.24, *J*=7 Hz, 3H).

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