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Intramolecular S_N^2 ring opening of a cyclic sulfate: synthesis of *erythro*-(−)-6-acetoxy-5-hexadecanolide — a major component of mosquito oviposition attractant pheromone †

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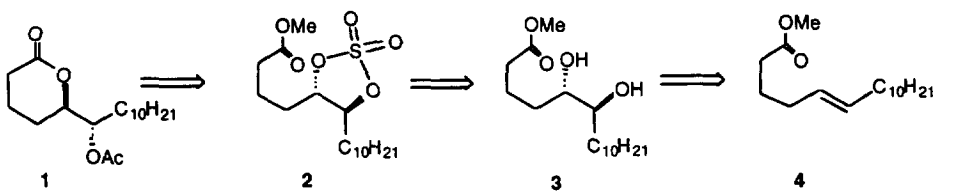
Abstract: Methyl *trans*-hexa-5-decenoate is dihydroxylated using AD-mix-α followed by treatment with thionyl chloride to furnish cyclic sulfite **8** as the major product. The cyclic sulfite **8** is oxidized to the cyclic sulfate **2**. Highly regio- and stereospecific ring opening of (4*S*,5*S*)-carboxybutyl-5-decylcyclic sulfate generated *in situ* by the hydrolysis of **2** furnished (5*R*,6*S*)-6-hydroxy-5-hexadecanolide **9** in high yield. Acetylation of **9** afforded natural oviposition attractant pheromone **1** in good yield.

Since the first isolation of a mosquito oviposition attractant pheromone in 1982,[1] several synthetic strategies have been developed for racemic and optically active *erythro*-6-acetoxy-5-hexadecanolide **1**.[2] The major interest in this class of compounds has been due to the need for safer pest control without the use of harmful insecticides or pesticides.[3] Several insect pheromones are in field trials and commercial use.[4]

In continuation of our interest to explore the usefulness of the asymmetric dihydroxylation (AD) reaction[5] and the stereoselective transformation of chiral diols *via* cyclic sulfites and cyclic sulfates,[6] we have developed a synthesis of (5*R*,6*S*)-6-acetoxy-5-hexadecanolide **1**. The synthetic strategy is outlined in Scheme 1. The salient feature of the present synthetic strategy is the highly regio- and stereoselective transformation of (4*S*,5*S*)-4-carboxybutyl-5-decyl-1,3,2-dioxathiolane 2,2-dioxide generated *in situ* from **2** to (5*R*,6*S*)-6-hydroxy-5-hexadecanolide **9** by inversion of the configuration at C_4.



1 **2** **3** **4**

Scheme 1. Retrosynthetic approach to the insect pheromone.

Such an intramolecular inversion of configuration has not been reported to the best of our knowledge in the case of cyclic sulfate chemistry, though several intermolecular openings of cyclic sulfates and cyclic sulfites are well documented.[6]

A mixture of *trans:cis* methyl 5-hexadecenoate **4** (19:81) was prepared by Wittig olefination of methyl 5-oxopentanoate **5**.[7] The *Z*-olefin was isomerized to predominantly the *E*-isomer to give a mixture of *E*:*Z* isomer in 83:17 ratio.[8] Asymmetric dihydroxylation of olefin **4** (*trans–cis* mixture) using OsO_4 in the presence of bis-9-*O*-dihydroquininyl phthalazine (DHQ_2-PHAL) as the chiral ligand

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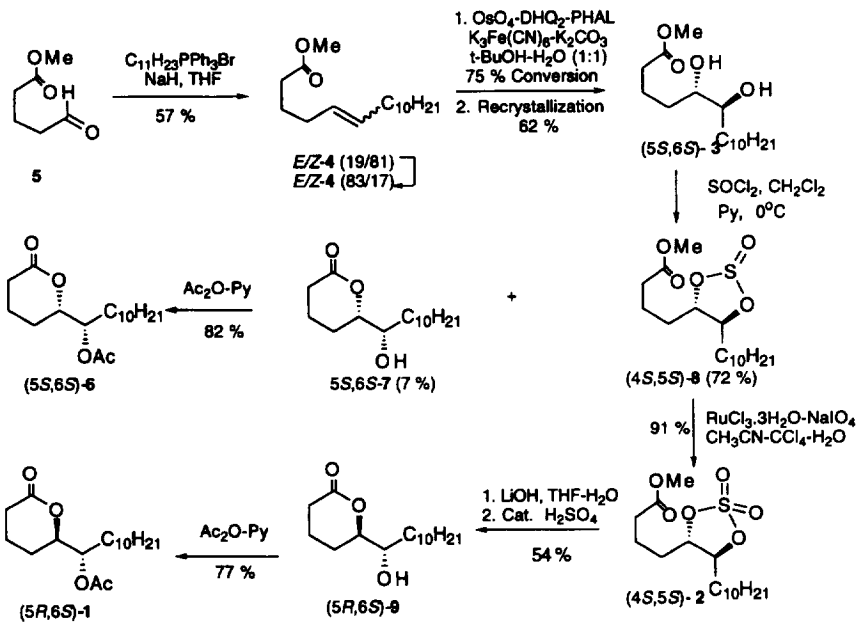
and $K_3Fe(CN)_6$–K_2CO_3 as the co-oxidant furnished methyl (5*S*,6*S*)-dihydroxyhexadecanoate **3**, in 62% yield. Since the *trans*-alkene undergoes relatively faster dihydroxylation, most of the *cis*-olefin can be removed unreacted after terminating the reaction at 75% conversion. The unreacted olefin **4** was isolated and examined by G.C. which shows the *cis*-isomer (*cis*:*trans*=83:17) to predominate (Scheme 2).



Scheme 2. Synthesis of insect pheromone **1** *via* cyclic sulfate.

The diol **3** was treated with thionyl chloride in CH_2Cl_2 in the presence of pyridine as base at *ca* 0°C to furnish two products, namely, sulfite **8** (72%), (*Rf* 0.95, EtOAc:Pet. ether 1:1) and another minor product (5*S*,6*S*)-6-hydroxy-5-hexadecanolide **7** (7%)(*Rf* 0.37, EtOAc:Pet. ether 1:1). The structures of **7** and **8** were determined based on spectral data. The structure of **7** was further confirmed by conversion to the corresponding (5*S*,6*S*)-6-acetoxy-5-hexadecanolide **6** and comparison of ^1H NMR spectral data with the reported values.[2m] The enantiomeric excess of **6** (82% ee) was determined by comparison of specific rotations. The cyclic sulfite **8** was oxidized to the cyclic sulfate **2** (91%), using $RuCl_3$–$NaIO_4$ in excellent yield.[6a] The methyl ester of cyclic sulfate **2** was hydrolysed with LiOH (1.5 eq) in THF–water (25:1) at room temperature to effect an intramolecular cyclization by the *in situ* generated carboxylate ion with concomitant S_N2 intramolecular ring opening of cyclic sulfate with inversion of configuration at the reacting center to furnish the sulfate salt. Hydrolysis of the sulfate salt with catalytic amount of conc. H_2SO_4 for 18 h furnished (5*R*,6*S*-)-6-hydroxy-5-hexadecanolide **9** (54% 83% ee). The hydroxylactone **9** was acetylated under standard condition using Ac_2O–Py to give 77% yield of pheromone **1** which was found to be identical in all respects to that of the natural mosquito oviposition attractant pheromone. Similarly, using AD-mix-β, we are able to prepare the optical antipode of 2-pyrone **6** and **1** in almost identical yield.

Conclusion

It has been possible to prepare the natural pheromone and its antipode in good yield using asymmetric dihydroxylation method followed by regio- and stereoselective intramolecular opening of the corresponding cyclic sulfate.

Experimental section

All mp and bp are uncorrected. Flash chromatography was carried out on silica gel SRL (230–400 mesh). TLC analysis was carried out on precoated Merck Kieselgel 60 F-254 plates. All solvents were distilled and dried before use. ^{1}H NMR spectra were recorded on a Varian Gemini (200 MHz) FT-NMR instrument in a $CDCl_3$ solution with TMS as the internal standard. ^{13}C spectra were recorded on the same instrument (50 MHz) in $CDCl_3$ solution. IR (υ_{max} in cm^{-1}) were recorded as neat or in solution on a Perkin Elmer 1600 series FT-IR spectrometer. Mass spectra were recorded on HP 5989A mass spectrometer and samples were introduced from LC through particle interface. Optical rotations were measured on JASCO DIP-370 digital polarimeter. Progress of the reaction was monitored by TLC. The *trans:cis* ratio was determined by gas chromatography using Shimadzu 17 AF gas chromatography.

*Methyl 5-hexadecenoate (*Z:E-***4***)*

To a magnetically stirred solution of undecyl triphenyl phosphonium bromide (1.0 g, 1.85 mmol) in tetrahydrofuran (3 mL) was added *n*-butyl lithium (1.5 mL, 1.2 M) at 0°C. The orange red coloured mixture was stirred at 0°C for 2 h. Methyl 5-oxopentanoate (200 mg, 1.54 mmol) was added to the reaction mixture at 0°C *via* a syringe and further stirred at 0°C for 4 h. The reaction was quenched with aqueous saturated ammonium chloride (10 mL) and the mixture was extracted with diethyl ether (2×15 mL) and the combined organic layer was washed with brine (2×10 mL), dried over sodium sulphate, filtered and evaporated. The residue was chromatographed over silica gel using 9.5:0.5 petroleum ether:ethyl acetate to give methyl 5-hexadecenoate (235 mg, 57%) as a colourless liquid. The gas chromatographic analysis showed a mixture of *cis* and *trans* olefin in 81:19 ratio. IR (Neat) υ_{max} 1743 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.6 Hz, 3 H), 1.2–1.3 (brs, 16 H), 1.6–1.8 (m, 2 H) 1.9–2.2 (m, 4 H), 2.25–2.4 (m, 2 H), 3.65 (s, 3 H), 5.2–5.5 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 24.8, 26.4, 27.1, 29.2, 29.5, 31.8, 33.3, 51.2, 128.2, 131.0, 173.9; Mass (% relative intensity) m/z 268 (M^+, 9), 236 (45), 194 (42), 166 (20), 152 (58), 123 (43), 110 (57), 96 (100), 87 (44).

*Isomerization of (*Z*)-***4*** to (*E*)-***4***

A mixture of methyl 5-hexadecenoate (*E* and *Z*-**4**; 19:81; 1 g, 3.73 mmol), thiophenol (300 mg, 2.72 mmol) and AIBN (100 mg, 0.609 mmol) in benzene (50 mL) was refluxed for 48 h. The reaction mixture was cooled, diluted with diethyl ether (50 mL), washed with water (20 mL), sodium bicarbonate solution (2×20 mL), brine (2×20 mL), dried over sodium sulfate, filtered and evaporated. The residue was chromatographed over silica gel using a mixture of 99:1 petroleum ether:ethyl acetate to give a mixture of *E* and *Z*-methyl 5-hexadecenoate **4** (955 mg, 96%) as a colorless liquid. The gas chromatographic analysis showed a mixture of *trans* and *cis* olefin in 83:17 ratio. IR (Neat) υ_{max} 1743 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.2 Hz, 3 H), 1.2–1.38 (brs, 16 H), 1.70 (quint, *J*=7.4 Hz, 2 H), 1.9–2.1 (m, 4 H), 2.31(t, *J*=7.4 Hz, 2 H), 3.67 (s, 3 H), 5.3–5.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.59, 24.65, 29.09, 29.26, 29.46, 29.55, 31.82, 32.47, 33.21, 51.17, 128.7, 131.57, 173.9; Mass (% relative intensity) m/z 268 (M, 4.6), 236 (37), 219 (13), 194 (48), 152 (34), 123 (27), 110 (42), 96 (100), 87 (33).

Methyl (5S,6S)-5,6-dihydroxyhexadecanoate ***3*** *(*E *and* Z*-***4***; 83:17)*

To a magnetically stirred solution of $K_3Fe(CN)_6$ (0.658 g, 2 mmol), K_2CO_3 (0.276 g, 2 mmol), DHQ_2–PHAL (20 mg, 0.025 mmol) in *t*-BuOH:H_2O (1:1, 10 mL) was added osmium tetroxide (10 μL, 0.5 M in toluene) followed by methane sulfonamide (71 mg, 0.75 mmol) and the mixture was stirred for 10 min at *ca.* 20°C. Methyl *trans* 5-hexadecenoate (*E* and *Z*-**4**; 268 mg, 1 mmol) was added at 0°C and the mixture was stirred at the same temperature. The reaction was followed by gas chromatography for nearly 75% conversion of alkene. Work-up of the reaction mixture and chromatography furnished the unreacted olefin (which was analysed by gas chromatography, *E* and *Z*-**4** olefin in 17:83 ratio) and methyl (5*S*,6*S*)-dihydroxyhexadecanoate **3** (0.187 g, 62%), mp 60–62°C, $[\alpha]_D^{23}$=−10.1 (c 1.0, $CHCl_3$); IR (KBr) υ_{max} 3357, 1734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J*=6.6 Hz, 3 H), 1.2–1.35

(brs, 16 H), 1.4–1.6 (m, 4 H), 1.7–1.9 (m, 2 H), 2.37 (t, J=7 Hz, 2 H), 3.35–3.45 (m, 2 H), 3.67 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.97, 20.90, 22.56, 25.60, 29.22, 29.52, 31.80, 32.81, 33.44, 33.70, 51.43, 73.83, 74.31, 174.2; Mass (% relative intensity) m/z 271 (0.8%), 253 (1.7), 235 (1.7), 131 (6.8), 100 (100), 99 (25), 87 (1.7). **(5*R*,6*R*)-Isomer-3:** As described above using $DHQD_2$–PHAL gave methyl 5*R*,6*R*-dihydroxy hexadecanoate (65% yield), mp 65–67°C; $[\alpha]_D^{25}$=+10.0 (c 1.01, $CHCl_3$).

(4S,5S)-Carbomethoxybutyl-5-decyl-1,3,2-dioxathiolane-2-oxide 8

In a round bottomed flask, methyl 5*S*,6*S*-dihydroxy hexadecanoate **3** (508 mg, 1.95 mmol) was dissolved in CH_2Cl_2 (5 mL) with stirring and pyridine (1.5 mL), and thionyl chloride (1.5 mL, 20.6 mmol) were added subsequently at *ca* 0°C. After 2 h, the reaction mixture was warmed up to *ca* 25°C and stirring was continued for additional 2 h. The mixture was then poured into ice cold water and extracted with chloroform (2×20 mL). The combined organic extracts were washed with 1N HCl, sodium bicarbonate, brine, dried over sodium sulfate and filtered. The solvent was evaporated under reduced pressure to furnish a residue which was chromatographed over silica gel using a mixture of ethyl acetate and petroleum ether (15:85) to give 420 mg (72%) of (4*S*,5*S*)-carbomethoxybutyl-5-decyl-1,3-dioxathiolane-2-oxide **8** $[\alpha]_D^{24}$=−42.3 (c 1.0, $CHCl_3$): IR (Neat) υ_{max} 1740, 1210, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3 H), 1.2–1.4 (brs, 16 H), 1.6–1.9 (m, 6 H), 2.41 (t, J=7 Hz, 2 H), 3.69 (s, 3 H), 4.0–4.1(m, 1 H), 4.5–4.65 (m, 1 H); Mass (% relative intensity) m/z 283 (M^+ -SO_2, 2%), 279 (2.5), 253 (11), 251 (18.5), 235 (17.5), 217 (16.5), 178 (35), 158 (40), 143 (66.5), 125 (47), 113 (20), 97 (65.5). Further elution of the column with a mixture of ethyl acetate and petroleum ether (40:60) furnished (5*S*,6*S*)-6-hydroxy-5-hexadecanolide **7** (31 mg, 7%; 82% ee), m.p. 66–69°C $[\alpha]_D^{25}$=+9.43 (c, 1.0, $CHCl_3$) (lit^{2m} $[\alpha]_D^{24}$=+11.5; c, 1.03, $CHCl_3$) IR (KBr) υ_{max} 3434, 1734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3 H), 1.2–1.4 (brs, 16 H), 1.5–1.7 (m, 3 H), 1.75–2.0 (m, 4 H), 2.4–2.7 (m, 2 H), 3.5–3.6 (m, 1 H), 4.1–4.25 (m, 1 H); Mass (relative intensity) m/z 269 (M-1,0.5%), 253 (2), 235 (2), 212 (1.5), 185 (3), 129 (5), 100 (100), 99 (31.5), 86 (12).

(4R,5R)-Carbomethoxybutyl-5-decyl-1,3,2-dioxathiolane 2-oxide

The reaction was performed as in the above case using methyl (5*R*,6*R*)-5,6-dihydroxyhexadecanoate (380 mg, 1.46 mmol) to furnish 320 mg (77%) of the corresponding cyclic sulfite $[\alpha]_D^{25}$=+49.3 (c, 1.0, $CHCl_3$) along with the corresponding (5*R*,6*R*)-6-hydroxy-5-hexadecanolide (20 mg, 6%; 94% ee); mp 69–70°C; $[\alpha]_D^{24}$=−9.68 (c, 1.0, $CHCl_3$) (lit^{2e} mp 70–71°C; $[\alpha]_D^{25}$=−10.2 (c, 0.87, $CHCl_3$).^{2m}

(5S,6S)-6-Acetoxy-5-hexadecanolide 6

To a solution of (5*S*,6*S*)-6-hydroxy-5-hexadecanolide **7** (20 mg, 0.074 mmol) in pyridine (0.5 mL) was added acetic anhydride (0.1 mL) at 0°C and the solution was allowed to stand overnight at *ca* 25°C. Work-up followed by chromatography over silica gel using a mixture of pet. ether:ethyl acetate (4:1) afforded a colorless oil (19 mg, 82%; 82% ee); $[\alpha]_D^{25}$=−11.5 (c, 0.7, $CHCl_3$) (lit^{2d} $[\alpha]_D^{25}$=−14.1); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3 H), 1.2–1.4 (brs, 16 H), 1.5–1.75 (m, 4 H), 1.8–2.0 (m, 2 H), 2.1 (s, 3 H), 2.4–2.7 (m, 2 H), 4.3–4.42 (m, 1 H), 4.95–5.05 (m, 1 H). **(5*R*,6*R*)-Isomer:** In the same manner as described above, (5*R*,6*R*)-6-hydroxy-5-hexadecanolide (20 mg, 0.07 mmol) gave (5*R*,6*R*)-6-acetoxy-5-hexadecanolide (18 mg, 77%; 95% ee) $[\alpha]_D^{25}$=+13.67 (c, 0.6, $CHCl_3$) (lit^{2e} $[\alpha]_D^{25}$=+14.4 (c, 1.06, $CHCl_3$).

(4S,5S)-Carbomethoxybutyl-5-decyl-1,3,2-dioxathiolane 2,2-dioxide 2

To a magnetically stirred solution of cyclic sulfite **8** (500 mg, 1.44 mmol) in CCl_4 (2 mL) and CH_3CN (2 mL) was added sodium metaperiodate (462 mg, 2.15 mmol) followed by ruthenium chloride (*ca* 2 mg) and water (3 mL). The mixture was stirred at *ca* 25°C for 2 h. The reaction mixture was diluted with ether (30 mL) organic layer was separated which was filtered through a bed of celite. The filtered organic layer was washed with water (2×10 mL) and sodium bicarbonate solution (10 mL) followed by brine (10 mL) and dried over sodium sulfate. The reaction mixture was filtered, evaporated and purified by column chromatography over silica gel using a mixture of petroleum ether:ethyl acetate

(4:1) to yield cyclic sulfate **2** as a colorless oil (475 mg, 91%); $[\alpha]_D^{26}=-28.82$ (c, 3.34, $CHCl_3$); IR (Neat) υ_{max} 1739, 1209 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.6 Hz, 3 H), 1.2–1.4 (brs, 16 H), 1.5–1.6 (m, 2 H), 1.7–1.9 (m, 4 H), 2.3–2.48 (m, 2 H), 3.7 (s, 3 H), 4.5–4.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.95. 20.49, 22.52, 25.03, 28.80, 29.13, 29.30, 30.96, 31.73, 32.78, 51.54, 86.88, 87.23, 172.93. Mass (% relative intensity) m/z 365 (M+1,12), 333 (89), 267 (23), 251 (60), 235 (27), 192 (48), 158 (62), 144 (64), 110 (71), 95 (100).

(4R,5R)-Isomer of cyclic sulfate

As described above, (4*R*,5*R*)-isomer (247 mg, 85%) was prepared from the corresponding cyclic sulfite (280 mg); $[\alpha]_D^{26}=+32.8$ (c, 1.0, $CHCl_3$).

(5R,6S)-6-Hydroxy-5-hexadecanolide ***9***

To an ice cold solution of cyclic sulfate **2** (60 mg, 0.164 mmol) in THF (0.5 mL) was added water (20 μL) followed by lithium hydroxide (10 mg, 0.24 mmol) and the solution was stirred for 18 h at 25°C then 2 h at 65–70°C. The reaction mixture was cooled and concentrated sulfuric acid (20 μL) was added and further stirred at 25°C for 16 h. The reaction mixture was diluted with diethyl ether (30 mL), washed with water, sodium bicarbonate solution, brine and dried over sodium sulfate. The solution was filtered, evaporated and purified by column chromatography over silica gel using a mixture of petroleum ether:ethyl acetate (6:4) to furnish (5*R*,6*S*)-6-hydroxy-5-hexadecanolide **9** (24 mg, 54%; 83% ee); mp 64–66°C; $[\alpha]_D^{25}=-10.4$ (c, 0.7, $CHCl_3$) (lit [2c] mp 67–68°C; $[\alpha]_D^{25}=-12.5$ (c, 0.54, $CHCl_3$); IR (KBr) υ_{max} 3430, 1717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.6 Hz, 3 H), 1.2–1.38 (brs, 16 H), 1.4–1.6 (m, 2 H), 1.75–2.1 (m, 5 H), 2.35–2.7 (m, 2 H), 3.79–3.9 (m, 1 H), 4.2–4.31 (m, 1 H). **(5*S*,6*R*)-Isomer**: As described above, (5*S*,6*R*)-isomer was prepared from the corresponding cyclic sulfate to give 51% yield of (5*S*,6*R*)-6-hydroxy-5-hexadecanolide (95% ee), mp 66–67°C; $[\alpha]_D^{25}=+12.0$ (c, 0.74, $CHCl_3$) (lit.[2c] mp 66.5–68°C, $[\alpha]_D^{25}=+12.7$ (c, 0.96, $CHCl_3$).

(5R,6S)-6-Acetoxy-5-hexadecanolide ***1***

As described earlier, (5*R*,6*S*)-6-hydroxy-5-hexadecanolide **9** (9 mg, 0.033 mmol) was acetylated using acetic anhydride (0.1 mL) in pyridine (0.25 mL) to furnish (5*R*,6*S*)-6-acetoxy-5-hexadecanolide **1** (8 mg, 77%; 81% ee); $[\alpha]_D^{25}=-31.5$ (c, 0.5, $CHCl_3$) (lit[2c] $[\alpha]_D^{25}=-38.5$ (c, 0.51, $CHCl_3$). IR (Neat) υ_{max} 1744 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.6 Hz, 3 H), 1.2–1.35 (brs, 16 H), 1.58–1.77 (m, 3 H), 1.8–2.0 (m, 3 H), 2.09 (s, 3 H), 2.35–2.7 (m, 2 H), 4.3–4.41 (m, 1 H), 4.91–5.05 (m, 1 H); Mass (% relative intensity) m/z 252 (M^+ –CH_3COOH), 235(2.5), 142(25), 100(28), 99(100). **(5*S*,6*R*)-Isomer**: As described above, (5*S*,6*R*)-6-hydroxy-5-hexadecanolide (15 mg) gave (5*S*,6*R*)-6-acetoxy-5-hexadecanolide (12 mg, 71%, 94% ee) as a colorless oil; $[\alpha]_D^{21}=+36.4$ (c, 1.2, $CHCl_3$) (lit[2c] $[\alpha]_D^{21}=+38.8$ (c, 1.21, $CHCl_3$).

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References

1. Laurence, B. R.; Pickett, J. A. *J. Chem. Soc. Chem. Commun.* **1982**, 59.
2. (a) For reviews, see Mori, K. *Tetrahedron* **1989**, *45*, 3233; (b) Masaki, Y.; Nagata, K.; Kaji, K. *Chem. Lett.* **1983**, 1835. (c) Mori, K.; Otsuka, T. *Tetrahedron* **1983**, *39*, 3267. (d) Lin G.-q.; Xu H.-J; Wu B.-C.; Guo G.-Z.; Zhou W.-S. *Tetrahedron Lett.* **1985**, *26*, 1233. (e) Ko, K.-Y.; Eliel, E. L. *J. Org. Chem.* **1986**, *51*, 5353. (f) Ochiai, M.; Ukita, T.; Iwaki, S.; Nagao, Y. S.; Fujita, E. *J. Org. Chem.* **1989**, *54*, 4832. (g) Kawamura, F.; Tayano, T.; Satoh, Y.; Hara, S.; Suzuki, A. *Chem. Lett.* **1989**, 1723. (h) Kang, S.-K.; Cho. I.-H. *Tetrahedron Lett.* **1989**, *30*, 743. (i) Rahman, S. S.; Wakefield, B. J.; Roberts, S. M.; Dowle, M. D. *J. Chem. Soc. Chem. Commun.* **1989**, 303. (j)

Prasit, P.; Rokach. J. *J. Org. Chem.* **1988**, *53*, 4422. (k) Sala, L. F.; Cravero, R. M.; Signorella, S. R.; Gonzalez-Sierra, M.; Ruveda, E. A. *Synth. Commun.* **1987**, *17*, 1287. (l) Kotsuki, H.; Kadota, I.; Ochi, M. *J. Org. Chem.* **1990**, *55*, 4417. (m) Gravier-Pelletier, C.; Le Merrer. Y.; Depezay, J.-C. *Tetrahedron* **1995**, *51*, 1663. (n) Bonini, C.; Checconi, M.; Righi, G.; Rossi, L. *Tetrahedron* **1995**, *51*, 4111.

3. Otieno, W. A.; Onyango, T. O.; Pile, M. M.; Laurence, B. R.; Dawson, G. W.; Wadhams, L. J.; Pickett, J. A. *Bull. Entomol. Res.* **1988**, *78*, 463.
4. Dawson, G. W.; Laurence, B. R.; Pickett, J. A.; Pile, M. M.; Wadhams, L. J. *Pestic. Sci.* **1989**, *27*, 277.
5. (a) Lohray, B. B. *Tetrahedron Asymmetry* **1992**, *3*, 1317. (b) Jayamma, Y.; Nandanan, E.; Lohray, B. B. *J. Indian Inst. Sci.* **1994**, *74*, 309. (c) Kolb, H. C.; Van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.
6. (a) Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538. (b) Lohray, B. B.; Gao, Y.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, *30*, 2623. (c) Lohray, B. B.; Ahuja, J. R. *J. Chem. Soc. Chem. Commun.* **1991**, 95. (d) Lohray, B. B.; Jayachandran, B.; Bhushan, V.; Ravindranathan, T.; *J. Org. Chem.* **1995**, *60*, 5983. (e) Lohray, B. B. *Synthesis* **1992**, 1035. (f) Lohray, B. B. and Bhushan, V. in *Advances in Heterocyclic Chemistry* in press.
7. Huckstep, M.; Taylor, R. J. K. *Synthesis* **1982**, 881.
8. Schwarz, M.; Graminski, G. F.; Waters, R. M. *J. Org. Chem.* **1986**, *51*, 260.

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