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A Concise Asymmetric Synthesis of (2*S*,3*S*,7*S*)-3,7-Dimethylpentadecan-2-yl Acetate and Propionate, the Sex Pheromones of Pine Sawflies

Pei-Qiang Huang,* Hong-Qiao Lan, Xiao Zheng, and Yuan-Ping Ruan

Department of Chemistry and The Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen, Fujian 361005, P. R. China

pqhuang@xmu.edu.cn

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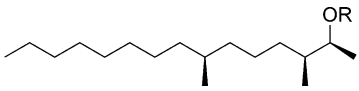
Abstract: (2*S*,3*S*,7*S*)-3,7-Dimethylpentadecan-2-yl acetate (**2**) and its propionate analogue (**3**) are the main sex pheromones of all *Neodiprion* species and *Diprion similes*, respectively. Starting from (*S*)-malic acid and employing a highly chemo-, regio-, and stereoselective tandem ester reduction−epoxide formation−reductive epoxide-opening reaction protocol, an efficient total synthesis of (2*S*,3*S*,7*S*)-**2** and -**3** is reported herein.

Pine sawflies (Hymenoptera: *Diprionidae*) are common insects widely distributed in the coniferous forests of Europe, Asia, and North American continents. They are considered to be severe pests on conifers. Since the pioneering work of Coppel, Jewett and co-workers,[1,2] it is known that the sex pheromones of several species of pine sawflies share a common alcohol moiety, namely 3,7-dimethylpentadecan-2-ol **1**; *Neodiprion lecontei* and *N. sertifer* uses acetate **2** as the major component of their pheromones, whereas *Diprion similis* uses propionate **3**.[2] Later studies revealed that the esters of the (2*S*,3*S*,7*S*)-3,7-dimethyl-2-pentadecanol (**1**) were the most active stereoisomers for all *Neodiprion* species.[3] Up to date, a number of methods[4−6] have been developed for the syntheses of stereoisomers[7] and homologous[7] of **1** in view of developing selective methods for monitoring and controlling the populations of these insects. However, only four asymmetric syntheses of (2*S*,3*S*,7*S*)-**1** have been reported.[6b−i] Most of the reported methods suffer from drawbacks such as necessity of resolution of the chiral intermediates,[6e] use of expensive nonnaturally occurring D-amino acids,[6g] too many synthetic steps, and/or low overall yields.



1. R=H
2. R=$COCH_3$
3. R=$COCH_2CH_3$

In connection with our interests in developing cheap and easily available (*S*)-malic acid as a chiral template for the asymmetric syntheses of bioactive molecules,[8] we now report a new approach to (2*S*,3*S*,7*S*)-**1** and its esters. Our approach to (2*S*,3*S*,7*S*)-**1** is depicted retrosynthetically in Scheme 1. The key to this approach was the synthesis of **6** and **7** starting from (*S*)-malic acid (**8**), which required an inversion of configuration at the chiral center of (*S*)-malic acid (**8**).

Although a stepwise approach could be considered for the conversion of (*S*)-malate **9** and (2*S*,3*R*)-3-methylmalate **17** to **6** and **7**, respectively,[9] we were interested in exploring a more efficient transformation based on an one-pot reaction. To this end, known dimethyl (*S*)-malate (**9**),[10] easily available from (*S*)-malic acid **8** in 98% yield, was treated with tosyl chloride−pyridine system to afford (*S*)-**10** in 97% yield (Scheme 2). Heating a suspension of (*S*)-**10** with 6 molar equiv of lithium aluminum hydride in THF afforded (+)-1,3-butanediol (**11**, yield 55%) and 1,4-butanediol (yield 15%). Comparing the optical rotation of the diol (+)-**11** [$[\alpha]^{20}_D$ +30.0 (*c* 1.0, EtOH)] with that of known (*S*)-enantiomer (+)-**11** [$[\alpha]^{20}_D$ +29.0 (*c* 1.0,

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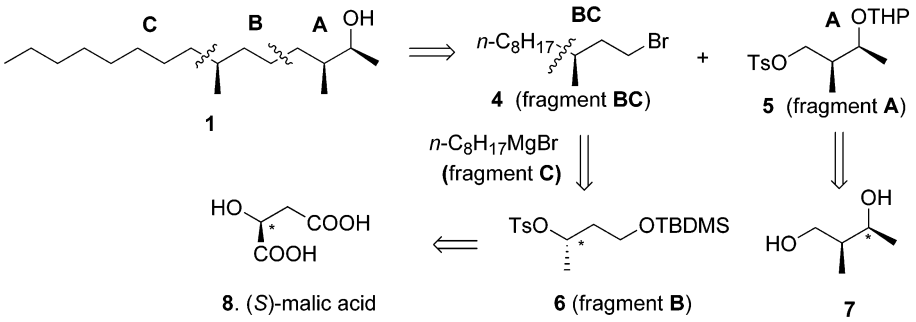
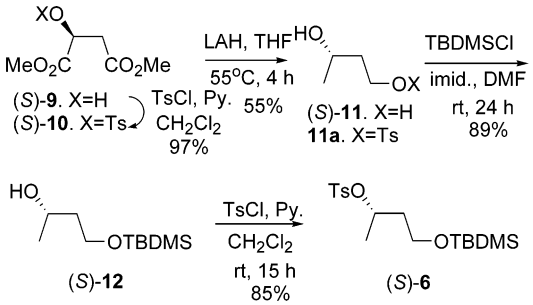
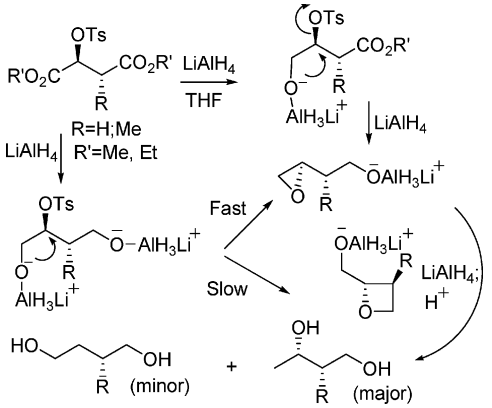
SCHEME 1. Retrosynthetic Analysis of 1



SCHEME 2. Synthesis of the Fragment B



SCHEME 3. Possible Mechanism of the One-Pot Reaction

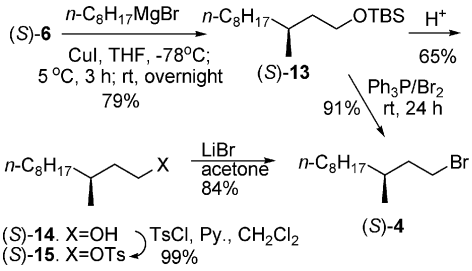


EtOH)][11] allowed its configuration to be assigned as *S*. Chiral HPLC analysis of the monotosylate **11a** showed that the *ee* of **11** was 97.3%. Selective monosilylation of (*S*)-**11** (TBDMSCl, imid, DMF) gave known (*S*)-**12**[12] in 89% yield, which was then tosylated to give the fragment **B** (**6**) in 85% yield.

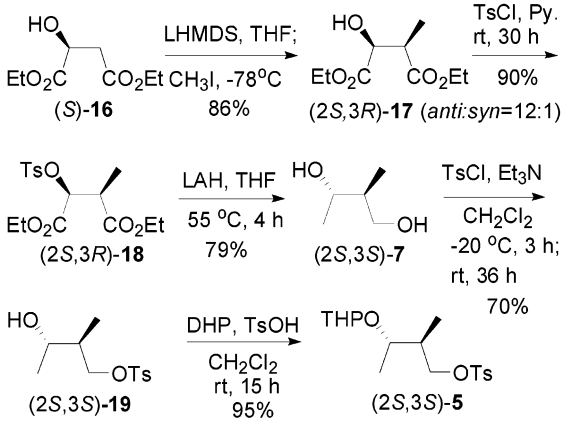
The stereoselective conversion of (*S*)-**10** to (*S*)-**11** implicates that an inversion of configuration occurred. A plausible mechanism for this transformation is depicted in Scheme 3, which involves sequential chemo- and regioselective ester reduction (or chemoselective ester reduction), S_Ni reaction with inversion of configuration (epoxide formation) and regioselective reductive epoxide-opening reaction at the terminal carbon.

Coupling of the organocopper species, generated in situ from *n*-C_8H_{17}MgBr (fragment **C**) and CuI in THF, with

SCHEME 4. Synthesis of the Fragment BC



SCHEME 5. Synthesis of the Fragment A



tosylate (*S*)-**6** (fragment **B**) proceeded smoothly to provide (*S*)-**13** in 79% yield (Scheme 4). (*S*)-**13** was then converted to bromide (*S*)-**4** [$[\alpha]^{20}_D$ +3.3 (*c* 5.1, hex.); lit.[6c] $[\alpha]^{20}_D$ +2.3 (neat); lit.[6e,7a] $[\alpha]^{20}_D$ +4.0 (*c* 4.5, hex.)] via a three-step procedure (HCl, 65%; TsCl, Py., 99%; LiBr, acetone, 84%). We were delighted to find that a one-pot transformation of **13** to **4** was possible, simply by treating **13** with PPh_3/Br_2.[13] In this way, **4** was obtained in 91% yield.

The synthesis of fragment **A** (**5**) began with **17**, easily available as an inseparable diastereomeric mixture (*anti*/*syn* = 12:1) from diethyl (*S*)-malate **16** (LHMDS, THF, −78 °C; MeI).[14] It was observed that using LHMDS in place of LDA as a base led to slightly improved diastereoselectivity (*anti*/*syn* = 12:1, combined yield: 86%) (Scheme 5). Tosylation of (2*S*,3*R*)-**17** gave **18** in 90% yield. It is worth noting that the tosylation of **17** not only provided the precursor for the key sequential reaction but rendered as well the separation of diastereomers

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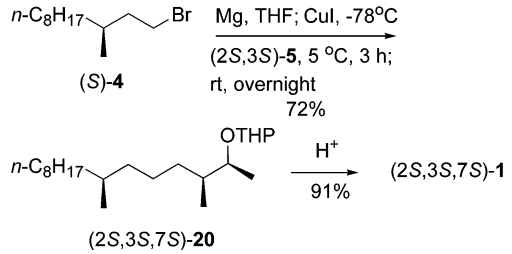
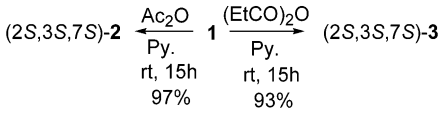
SCHEME 6. Synthesis of (2*S*,3*S*,7*S*)-1



SCHEME 7. Synthesis of 2 and 3



possible. Thus, treatment of pure *anti*-**18** with LAH (6 molar equiv) in THF afforded the desired diol **7**[15] [colorless oil, $[\alpha]^{20}_D$ +10.6 (*c* 1.1, $CHCl_3$)] in 79% yield and 2-methyl-1,4-butanediol in 10% yield. Selective monotosylation of **7** followed by protection of the secondary hydroxyl group yielded known fragment **A** (**5**)[6e] as a diastereomeric mixture at the acetal carbon. Chiral HPLC analysis of (2*S*,3*S*)-**19** showed that the enantiomeric excess of **7** was 98.1%.

With the fragments **A** and **BC** available, their coupling[6e,16] were undertaken. Thus, treatment of organometallic species (fragment **BC**) generated from bromide **4** (Mg/THF; CuI) with tosylate **5** gave desired **20** in 72% yield (Scheme 6). Finally, deprotection of **20** under acidic conditions afforded (2*S*,3*S*,7*S*)-3,7-dimethyl-2-pentadecanol (**1**) [colorless oil, $[\alpha]^{20}_D$ −9.9 (*c* 4.0, hexane) [lit.[6b,c] $[\alpha]^{20}_D$ −9.8 (neat); lit.[6e] $[\alpha]^{20}_D$ −10.4 (*c* 3.7, hexane); lit.[6d] $[\alpha]^{20}_D$ −12.2 (neat); lit.[6f] $[\alpha]^{23}_D$ −9.6 (*c* 0.65, hexane); lit.[6g] $[\alpha]^{20}_D$ −11.5 (*c* 0.8, hexane); lit.[6i] $[\alpha]^{20}_D$ −11.8 (neat)]], the common alcohol moiety of the sex pheromones of the pine sawflies, in 91% yield. Spectral properties of our synthetic **1** were identical with those of the natural compound.[6]

Finally, acylation of **1** afforded the sex pheromone **2** [colorless oil, $[\alpha]^{20}_D$ −5.7 (*c* 1.3, hex.) [lit.[6b,6c] $[\alpha]^{20}_D$ −5.8 (neat); lit.[6e] $[\alpha]^{20}_D$ −6.0 (*c* 4.3, hex.)]] in 97% yield (Scheme 7). Similarly, propionation of **1** with propionic anhydride furnished **3** [colorless oil, $[\alpha]^{20}_D$ −5.7 (*c* 0.6, hexane) [lit.[6b,6c] $[\alpha]^{20}_D$ −5.5 (neat); lit.[6e] $[\alpha]^{20}_D$ −6.9 (*c* 18, hex.)]] in 93% yield.

In summary, starting from (*S*)-malic acid, an efficient total synthesis of (2*S*,3*S*,7*S*)-3,7-dimethylpentadecan-2-yl acetate (**2**) and propionate (**3**), the active enantiomers of the pheromones of pine sawflies, was achieved. The synthesis features tandem ester reduction−epoxide formation−reductive epoxide−opening reaction [(*S*)-**10** → (*S*)-**11** and (2*S*,3*R*)-**18** → (2*S*,3*S*)-**7**] as the key steps. This one-pot, chemo-, regio- and stereoselective transformation is not only highly efficient, but also proceeds with inversion of configuration, allowing the establishment of all the three chiral centers of (2*S*,3*S*,7*S*)-**1** from L-malic acid.

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Experimental Section

(*S*)-1,3-Butanediol (11). To a suspension of LAH (2.06 g, 54.3 mmol) in anhydrous THF (100 mL) was added dropwise a solution of **10** (2.91 g, 9.22 mmol) in THF (8.0 mL) The mixture was stirred at 55 °C for 4 h and then re-cooled to −20 °C. To the resultant mixture were added successively water (2.8 mL), 15% NaOH (2.8 mL), and water (8.4 mL). The mixture was filtered through Celite. The filtrate was concentrated in vacuo and the residue was chromatographed (eluent: EtOAc) to afford (*S*)-**11** (colorless oil, 456 mg, yield 55%) and 1,4-butanediol (124 mg, yield 15%). (*S*)-**11**: $[\alpha]^{20}_D$ +30.0 (*c* 1.0, EtOH) [lit.[11] $[\alpha]^{20}_D$ +29.0 (*c* 1.0, EtOH) for (*S*)-**11**]; IR (film) 3337, 1458, 1376, 1288, 1261, 1075, 1053 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (d, J = 6.3 Hz, 3H), 1.70 (m, 2H), 3.05 (s, br, 2H), 3.81 (ddd, J = 5.7, 5.7, 10.8 Hz, 1H), 3.88 (ddd, J = 5.2, 5.2, 10.8 Hz, 1H), 4.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.8, 40.0, 61.6, 68.1. MS (ESI) *m*/*z* 91 (M + H^+, 100); HRMS *m*/*z* calcd for $C_8H_{21}O_4^+$ (2M + H^+) 181.1440, found 181.1434. Chiral HPLC analysis of both racemic **11a** and (*S*)-**11a** using a CHIRALPAK column (hex./EtOH = 6/4, t_R = 9.44 min for *S*-enantiomer; t_R = 8.81 min. for *R*-enantiomer) showed that the ee of (*S*)-**11** was 97.3%.

(2*S*,3*S*)-2-Methyl-1,3-butanediol (7). Following the procedure described for the conversion of **10** to **11**, **18** was converted to **7** in a yield of 79%. (*R*)-2-Methyl-1,4-butanediol was also obtained in a yield of 10%. (2*S*,3*S*)-**7**:[15] colorless oil; $[\alpha]^{20}_D$ +10.6 (*c* 1.1, $CHCl_3$); IR (film) 3337, 1730, 1653, 1458, 1376, 1288, 1261, 1132, 1075, 1053, 1008 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.4 Hz, 3H), 1.80 (m, 1H), 2.52 (s, br, 1H), 2.60 (s, br, 1H), 3.68 (m, 2H), 4.02 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.7, 19.5, 40.1, 66.6, 70.8; MS (ESI) *m*/*z* 127 (M + Na^+, 100), 105 (M + H^+, 32); HRMS *m*/*z* calcd for $C_{15}H_{25}O_4^+$ (2M + H^+) 209.1753, found 209.1744.

(2*S*,3*S*)-2-Methyl-1-(*p*-toluenesulfonyloxy)-3-butanol (19). To a solution of (2*S*,3*S*)-**7** (68 mg, 0.65 mmol) in CH_2Cl_2 (0.5 mL) was added Et_3N (0.12 mL, 0.81 mmol) at −20 °C. To the mixture was added a solution of TsCl (124 mg, 0.65 mmol) in CH_2Cl_2 (0.5 mL) over 2 h. After being stirred at −20 °C for 3 h, the mixture was allowed to warm and stirred for an additional 36 h. The mixture was poured into 1.2 mL of water and extracted with CH_2Cl_2. The organic layers were washed successively with an aqueous solution of 2 N HCl (0.5 mL), a saturated aqueous solution of $NaHCO_3$ (0.5 mL) and brine (0.5 mL), dried ($MgSO_4$), and concentrated. The residue was chromatographed (eluent: EtOAc/PE = 1: 4) to give **19** (118 mg, yield: 70%) as a colorless oil, $[\alpha]^{20}_D$ +3.2 (*c* 1.1, $CHCl_3$). Chiral HPLC analysis under the conditions described for racemic **11a** showed that the *ee* of **19** was 98.1%: IR (film) 3552, 3426, 2975, 2929, 1598, 1458, 1356, 1177, 1097 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.82 (d, J = 7.1 Hz, 3H), 1.09 (d, J = 6.2 Hz, 3H), 1.67 (s, br, 1H), 1.79 (m, 1H), 2.42 (s, 3H), 3.86 (m, 2H), 4.01 (m, 1H), 7.35 (m, 2H), 7.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.9, 20.3, 21.6, 39.0, 66.8, 72.6, 127.9, 127.9, 129.9, 129.9, 132.9, 144.8; MS (ESI) *m*/*z* 276 (M^+ + H_2O, 100%); HRMS *m*/*z* calcd for $C_{12}H_{19}SO_4^+$ (M + H^+) 259.1004, found 259.0997.

(2*S*,3*S*,7*S*)-3,7-Dimethyl-2-pentadecanol (1). A mixture of **19** (570 mg, 2.21 mmol), dihydropyran (0.30 mL, 2.67 mmol), and a catalytic amount of *p*-toluenesulfonic acid in dry CH_2Cl_2 (9.0 mL) was stirred at rt overnight. The mixture was quenched with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (eluent: EtOAc/PE = 1:10), and known **5**[3a,6e,7b] (718 mg, yield 95%) was obtained as a colorless oil.

Grignard reagent, prepared from magnesium (53 mg, 2.21 mmol) and (*S*)-**4** (548 mg, 2.20 mmol) in anhydrous THF (5.0 mL) under argon atmosphere, was chilled to −78 °C. A solution of (2*S*, 3*S*)-**5** (343 mg, 1.0 mmol) in THF (2.0 mL) and CuI (cat.) were added. The reaction mixture was allowed to warm to 5 °C and stirred at that temperature for 3 h. After being stirred overnight at rt, the reaction mixture was cooled with an ice bath and then poured into ice-cooled aqueous NH_4Cl and extracted with ether. The combined ethereal solution was washed successively with aqueous NH_4Cl, aqueous $NaHCO_3$ and brine, dried

(Na_2SO_4), and concentrated. After flash chromatographic purification (eluent: EtOAc/PE = 1:50), known **20**[3a,6e,7b] (245 mg, yield 72%) was obtained as a colorless liquid.

A methanolic solution (8.0 mL) of **20** (245 mg, 0.72 mmol) was stirred in the presence of a catalytic amount of *p*-toluenesulfonic acid at rt for 24 h. The resultant mixture was concentrated under reduced pressure. The resulted residue was purified by flash chromatography (eluent: EtOAc/PE = 1:10) to afford (2*S*,3*S*,7*S*)-3,7-dimethyl-2-pentadecanol (**1**) (168 mg, yield: 91%) as a colorless oil: $[\alpha]\ ^{20}_D$ −9.9 (*c* 4.0, hex.) [lit.[6e] $[\alpha]^{20}_D$ −10.4 (*c* 3.7, hex.); lit.[6f] $[\alpha]^{23}_D$ −9.6 (*c* 0.65, hex.); lit.[6g] $[\alpha]^{20}_D$ −11.5 (*c* 0.8, hex.); lit.[6i] $[\alpha]^{20}_D$ −11.8 (neat)]; IR (film) 3373, 2925, 2855, 1463, 1377, 1322, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H), 0.89 (d, J = 6.3 Hz, 3H), 1.15 (d, J = 6.4 Hz, 3H), 1.0−1.7 (m, 23H), 3.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 14.2, 19.8, 20.3, 22.7, 24.8, 27.1, 29.4, 29.7, 30.1, 32.0, 32.8, 33.0, 37.0, 37.4, 39.8, 71.4; MS (ESI) *m*/*z* 274 ($M^+ + H_2O$, 52), 279 ($M + Na^+$, 100). GC analysis showed that the purity of **1** was 99.5%.

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Supporting Information Available: Experimental procedures and spectral data for compounds **2**−**4**, **6**, **10**, **12**−**15**, **18**; ^1H NMR and ^{13}C NMR spectra of **1**−**4**, **6**, **7**, **13**−**15**, **18**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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