Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 1451–1456

TETRAHEDRON: *ASYMMETRY*

A furan route to (−)-*exo*-isobrevicomin

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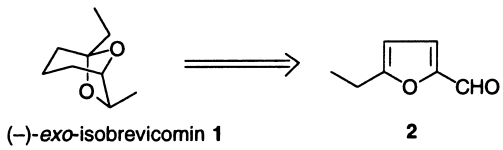
Received 5 March 1998; accepted 18 March 1998

Abstract

A new enantiocontrolled synthesis of (−)-*exo*-isobrevicomin, isolated from male mountain pine beetles, *Dendroctonus ponderosae*, has been established starting from 5-ethyl-2-furfural by employing AD-mix-induced asymmetric induction and oxidative furan ring-expansion reaction as the key steps. © 1998 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

(−)-*exo*-Isobrevicomin **1**, (1*S*,5*R*,7*S*)-5-ethyl-7-methyl-6,8-dioxabicyclo[3.2.1]octane, was isolated from male mountain pine beetles, *Dendroctonus ponderosae* in 1996 by Francke and co-workers[1] and determined by the synthesis starting from (+)-tartaric acid.[1] Later in 1997, Mori and co-workers synthesized it in enantiomerically pure form through a sequence of steps involving the Sharpless asymmetric dihydroxylation (AD reaction), which attained 75% ee with enantiomeric purification steps *via* recrystallization.[2,3] We wish to report here an alternative synthesis of (−)-*exo*-isobrevicomin **1** starting from 5-ethyl-2-furfural **2** by employing the AD reaction[4] and oxidative furan ring-expansion reaction[5,6] as the key steps. Although the present synthesis employed the same AD reaction to induce asymmetry as in Mori's synthesis, the optical induction was raised to 97.5% ee probably due to the molecular background of the substrate[2] (Scheme 1).



(−)-*exo*-isobrevicomin **1** **2**

Scheme 1.

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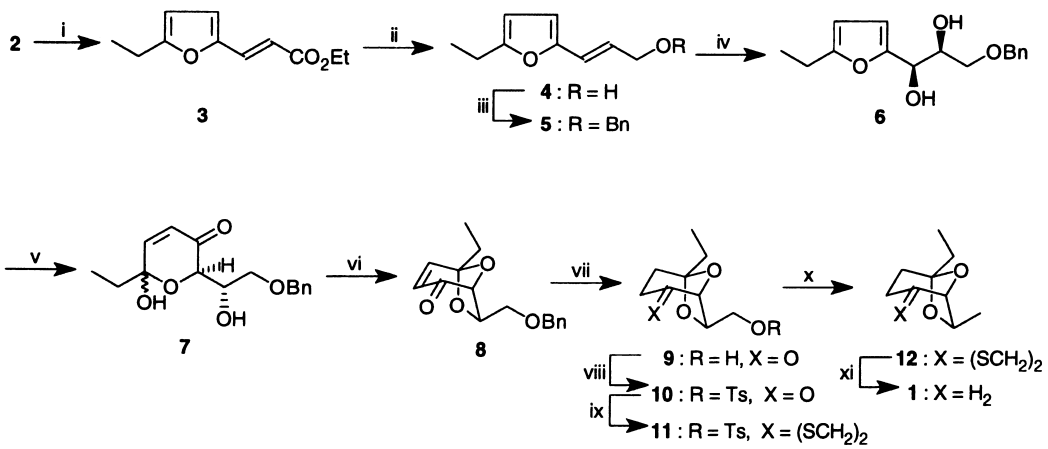
PII: S0957-4166(98)00117-7

2. Results and discussion

Horner–Emmons reaction of 5-ethyl-2-furfural **2** with ethyl diethylphosphonoacetate in the presence of sodium hydride afforded the (*E*)-α,β-unsaturated ester **3** stereoselectively in 96% yield. Reduction of **3** with diisobutylaluminum hydride (DIBAL) followed by alkylation of the resulting allylic alcohol **4** with benzyl bromide gave the allyl benzyl ether **5** in excellent overall yield. The ether **5** was then subjected to the AD reaction[6] using a commercially available AD-mix-α reagent[7] under standard conditions in the presence of methanesulfonamide[4] to give the optically active 1,2-glycol **6** in 93% yield. As its optical purity could not be determined at this stage, **6** was oxidized with *m*-chloroperbenzoic acid (*m*CPBA) to initiate the ring-expansion to give the 3-pyranone **7** as a mixture of two epimers which, without separation, was acid-cyclized to give the bicyclic enone **8** having a 6,8-dioxabicyclo[3.2.1]octane framework in 64% overall yield as a single isomer. Enantiomeric excess of **8** was determined at this stage as 97.5% ee by hplc using a chiral column (CHIRALCEL OJ). As no enantiomer purification was involved during the transformation, it was assumed that the enantiomeric excess of **8** directly reflected the chiral integrity of the 1,2-glycol **6**. The high enantioselectivity was presumed to be due to the presence of the furan ring, as simple *trans*-substituted olefins, as appeared in the Mori's synthesis,[2] did not exhibit such high induction.[4]

Having determined the enantiomeric excess, **8** was hydrogenated on 10% palladized carbon in ethyl acetate under hydrogen under atmospheric pressure to give the keto-alcohol **9**, in excellent yield, by concurrent hydrogenation and hydrogenolysis. To remove the hydroxy and the ketone oxygen functionalities, **9** was sequentially tosylated and thioketalized to give the tosyl-dithiolane **11** *via* **10** in a satisfactory overall yield. Treatment of **11** with lithium aluminum hydride (LAH) led to reductive removal of the tosyloxy group to give **12** whose dithiolane group was then removed with Raney nickel[8] to give (−)-*exo*-isobrevicomin **1**. Overall yield of (−)-*exo*-isobrevicomin **1** from 5-ethyl-2-furfural **2** was 17% in 11 steps. Its enantiomeric excess estimated by comparison with Mori's specific rotation value[2] was 92.5% ee though a higher ee value could be expected based on the enantiomeric excess of the intermediate **6** determined by hplc analysis (Scheme 2).



Scheme 2. *Reagents and conditions*: (i) $(EtO)_2POCH_2CO_2Et$, NaH, THF, 96%; (ii) DIBAL, CH_2Cl_2, 97%; (iii) BnBr, NaH, THF:DMF (1:1), 97%; (iv) AD-mix-α, $MeSO_2NH_2$, *tert*-BuOH:H_2O (1:1), 93%; (v) *m*CPBA, CH_2Cl_2; (vi) *p*TsOH, benzene, 63% from **6**; (vii) H_2, 10% Pd–C, AcOEt, 96%; (viii) *p*TsCl, Et_3N, DMAP, CH_2Cl_2, 96%; (ix) $(CH_2SH)_2$, $BF_3 \cdot OEt_2$, CH_2Cl_2, 79%; (x) LAH, THF, 79%; (xi) Raney Ni, EtOH, 56%

In summary, a combination of AD reaction and oxidative furan-ring expansion reaction allowed construction of (−)-*exo*-isobrevicomin in high enantiomeric excess and in satisfactory overall yield.

3. Experimental

IR spectra were recorded on a JASCO-IR 700 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-2000 (300 MHz) spectrometer. Optical rotations were measured with a JASCO-DIP 370 digital polarimeter. Optical purities were determined on a Gilson Model-307 instrument equipped with a chiral column.

3.1. *Ethyl (*E*)-3-(5-ethylfurfuryl)prop-2-enoate* ***3***

To a stirred suspension of NaH (60% oil dispersion, 820 mg, 20.5 mmol) in THF (40 ml) was added ethyl diethylphosphonoacetate (4.74 ml, 23.9 mmol) and **2**[7] (2.12 g, 17.1 mmol) in THF (20 ml) was added at 0°C. After stirring for 10 min at the same temperature, the reaction was quenched by addition of water and the mixture was extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, evaporated under reduced pressure, and chromatographed (SiO_2, 45 g, elution with AcOEt:hexane=1:20 v/v) to give the unsaturated ester **3** (3.18 g, 96%) as a pale yellow oil. IR (film): ν=1706, 1637 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=7.37 (d, 1H, *J*=15.7 Hz), 6.51 (d, 1H, *J*=3.3 Hz), 6.24 (d, 1H, *J*=15.7 Hz), 6.08 (dt, 1H, *J*=3.3, 0.8 Hz), 4.23 (q, 2H, *J*=7.1 Hz), 2.68 (q, 2H, *J*=7.5 Hz), 1.32 (t, 3H, *J*=7.1 Hz), 1.26 (t, 3H, *J*=7.5 Hz). HRMS: calcd for $C_{11}H_{14}O_3$: 194.0943. Found: 194.0939. Anal. calcd for $C_{11}H_{14}O_3$: C 68.02, H 7.26. Found: C 67.84, H 7.34.

3.2. *(*E*)-3-(5-Ethyl-2-furfuryl)prop-2-en-1-ol* ***4***

To a stirred solution of **3** (3.08 g, 15.8 mmol) in CH_2Cl_2 (60 ml) was added dropwise DIBAL (1.5 M in toluene: 26.4 ml, 39.6 mmol) at −78°C. After stirring for 5 h at the same temperature, the reaction was quenched by addition of H_2O (26.4 ml). After stirring for 1 h at room temperature, the mixture was extracted with EtO_2. The extract was washed with brine, dried over $MgSO_4$, evaporated under reduced pressure, and chromatographed (SiO_2, 65 g, elution with AcOEt:hexane=1:3 v/v) to give **4** (2.33 g, 97%) as a pale yellow oil. IR (film): ν=3342, 1659 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=6.38 (d, 1H, *J*=15.9 Hz), 6.22 (dt, 1H, *J*=15.9, 5.8 Hz), 6.14 (d, 1H, *J*=3.2 Hz), 5.96 (dt, 1H, *J*=3.2, 0.5 Hz), 4.28 (t, 2H, *J*=5.8 Hz), 2.65 (q, 2H, *J*=7.7 Hz), 1.50 (br s, 1H), 1.24 (t, 3H, *J*=7.7 Hz). HRMS: calcd for $C_9H_{12}O_2$: 152.0837. Found: 152.0806.

3.3. *(*E*)-1-Benzyloxy-3-(5-ethyl-2-furfuryl)prop-2-ene* ***5***

To a stirred solution of **4** (1.17 g, 7.70 mmol) in a mixture of DMF and THF (1:1 v/v, 30 ml) was added NaH (60% oil dispersion, 400 mg, 10.0 mmol) at 0°C. After stirring for 10 min at the same temperature, to the mixture was added benzyl bromide (1.28 ml, 10.8 mmol) at the same temperature and the stirring was continued for 10 h at room temperature. The reaction was quenched by addition of water and the organic layer was separated. The organic layer was washed with brine, dried over $MgSO_4$, evaporated under reduced pressure and chromatographed (SiO_2, 25 g, elution with AcOEt:hexane=1:200 v/v) to give **5** (1.81 g, 97%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ=7.38–7.28 (m, 5H), 6.39 (dt, 1H, *J*=15.7, 1.4 Hz), 6.18 (dt, 1H, *J*=15.7, 6.0 Hz), 6.13 (d, 1H, *J*=3.0 Hz), 5.96 (dt, 1H, *J*=3.0, 1.1 Hz), 4.56 (s, 2H), 4.15 (dd, 2H, *J*=6.0, 1.4 Hz), 2.64 (q, 2H, *J*=7.5 Hz), 1.23 (t, 3H, *J*=7.5 Hz). HRMS: calcd for $C_{16}H_{18}O_2$: 242.1307. Found: 242.1312.

3.4. (1R,2S)-3-Benzyloxy-1-(5-ethyl-2-furfuryl)-1,2-dihydroxypropane **6**

To a stirred solution of **5** (1.81 g, 7.48 mmol) and $MeSO_2NH_2$ (712 mg, 7.48 mmol) in aqueous *tert*-BuOH (50%, 50 ml) was added AD-mix-α (10.4 g) at 0°C and the mixture was stirred for 61 h at the same temperature. The reaction was quenched by addition of Na_2SO_3 (2.83 g, 22.5 mmol) and the mixture, after 10 min at room temperature, was separated. The organic layer was washed successively with 10% KOH and brine, dried over $MgSO_4$, evaporated under reduced pressure, and chromatographed (SiO_2, 40 g, elution with AcOEt:hexane=1:3 v/v) to give (1*R*,2*R*)-**6** (1.92 g, 93%) as a pale yellow oil: $[\alpha]_D^{30}$ −17.73 (*c* 1.23, $CHCl_3$). IR (film): ν=3416 cm^{-1}. ^1H NMR ($CDCl_3$): δ=7.38–7.30 (m, 5H), 6.21 (d, 1H, *J*=3.2 Hz), 5.92 (dt, 1H, *J*=3.2, 1.1 Hz), 4.69 (d, 1H, *J*=5.8 Hz), 4.54 (d, 2H, *J*=5.8 Hz), 4.09 (td, 1H, *J*=5.8, 3.7 Hz), 3.58 (dd, 1H, *J*=9.9, 3.7 Hz), 3.49 (dd, 1H, *J*=9.9, 5.8 Hz), 2.89 (br s, 1H), 2.78 (br s, 1H), 2.62 (q, 2H, *J*=7.5 Hz), 1.21 (t, 3H, *J*=7.5 Hz). HRMS: calcd for $C_{16}H_{20}O_4$: 276.1361. Found: 276.1363. Anal. calcd for $C_{16}H_{20}O_4$: C 69.55, H 7.29. Found: C 69.36, H 7.30.

3.5. (1R,5R,7S)-7-Benzyloxymethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]-oct-3-en-2-one **8**

To a stirred solution of **6** (965 mg, 3.49 mmol) in CH_2Cl_2 (30 ml) was added *m*CPBA (70%, 948 mg, 3.84 mmol) at 0°C and the mixture was stirred at 0°C for 10 min and at room temperature for 3 h. The mixture was filtered through a Celite pad and evaporated to give a residue containing **7** which was dissolved in benzene (30 ml) and refluxed with *p*-toluenesulfonic acid (6.65 mg, 0.03 mmol) with removal of water using a Dean–Stark apparatus. The mixture was washed with 5% aqueous $NaHCO_3$, brine, dried over $MgSO_4$, evaporated under reduced pressure, and chromatographed (SiO_2, 20 g, elution with Et_2O:hexane=1:5 v/v) to give **8** (613 mg, 64%) as a pale yellow oil: $[\alpha]_D^{31}$ +158.64 (*c* 1.26, $CHCl_3$). IR (film): ν=1700 cm^{-1}. ^1H NMR ($CDCl_3$): δ=7.36–7.29 (m, 5H), 7.00 (d, 1H, *J*=9.8 Hz), 6.06 (dd, 1H, *J*=9.8, 1.5 Hz), 4.59 (s, 2H), 4.55 (t, 1H, *J*=1.1 Hz), 4.00 (ddd, 1H, *J*=6.6, 5.9, 1.1 Hz), 3.62 (dd, 1H, *J*=9.9, 5.9 Hz), 3.50 (dd, 1H, *J*=9.9, 6.6 Hz), 1.97 (qd, 2H, *J*=7.5, 1.5 Hz), 1.04 (t, 3H, *J*=7.5 Hz). ^{13}C NMR (75 MHz) $CDCl_3$: δ=194.8, 150.6, 128.6, 127.9, 127.8, 126.6, 105.9, 82.5, 74.1, 73.4, 70.1, 27.8, 6.7. HRMS: Calcd for $C_{16}H_{18}O_4$: 274.1205. Found: 274.1181. Anal. calcd for $C_{16}H_{18}O_4$: C 70.06, H 6.61. Found: C 69.94, H 6.58. Optical purity was determined to be 97.5% ee by HPLC using a chiral column (CHIRALCEL OJ, elution with Pr^iOH:hexane=2:98 v/v).

3.6. (1R,5R,7S)-5-Ethyl-7-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octan-2-one **9**

A solution of **8** (957 mg, 3.49 mmol) in AcOEt (20 ml) was hydrogenated in the presence of 10% Pd–C (10 mg) under an atmospheric pressure of hydrogen at room temperature for 24 h. After removal of the catalyst by filtration, the filtrate was evaporated under reduced pressure and chromatographed (SiO_2, 20 g, elution with AcOEt:hexane=1:2 v/v) to give **9** (624 mg, 96%) as a pale yellow oil: $[\alpha]_D^{26}$ −40.29 (*c* 1.06, $CHCl_3$). IR (film): ν=3442, 1730 cm^{-1}. ^1H NMR ($CDCl_3$): δ=4.31 (s, 1H), 4.16 (t, 1H, *J*=6.2 Hz), 3.62 (d, 2H, *J*=6.2 Hz), 2.55–2.48 (m, 2H), 2.35 (br s, 1H), 2.21–2.03 (m, 2H), 1.88 (qd, 2H, *J*=7.5, 2.3 Hz), 1.03 (t, 3H, *J*=7.5 Hz). HRMS: calcd for $C_9H_{14}O_4$: 186.0892. Found: 186.0889.

3.7. (1R,5R,7S)-5-Ethyl-7-[p-toluenesulfonyloxymethyl]-6,8-dioxabicyclo[3.2.1]octan-2-one **10**

To a stirred solution of **9** (664 mg, 3.53 mmol) in CH_2Cl_2 (10 ml) was added Et_3N (984 μl, 7.06 mmol), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (43 mg, 0.35 mmol), and *p*-toluenesulfonyl chloride (1.01 g, 5.29 mmol) at room temperature and the mixture was stirred for 6 h at the same temperature. The mixture

was washed with brine, dried over $MgSO_4$, evaporated under reduced pressure, and chromatographed (SiO_2, 15 g, elution with Et_2O:hexane=1:3 v/v) to give **10** (1.15 g, 96%) as a pale yellow oil: $[\alpha]_D^{28}$ −27.65 (*c* 0.88, $CHCl_3$). IR (film): ν=1733, 1366, 1177 cm^{-1}. ^1H NMR ($CDCl_3$): δ=7.80 (d, 2H, *J*=8.5 Hz), 7.37 (d, 2H, *J*=8.5 Hz), 4.25 (s, 1H), 4.21 (dd, 1H, *J*=7.2, 5.7 Hz), 3.99 (dd, 1H, *J*=10.0, 5.7 Hz), 3.90 (dd, 1H, *J*=10.0, 7.2 Hz), 2.50–2.45 (m, 5H), 2.11–2.01 (m, 2H), 1.79 (qd, 2H, *J*=7.5, 3.8 Hz), 0.92 (t, 3H, *J*=7.5 Hz). HRMS: calcd for $C_{16}H_{20}O_6S$: 340.0980. Found: 340.1000.

*3.8. (1*R,*5*R,*7*S*)-5-Ethyl-2-(1,3-dithiolane)-7-[*p*-toluenesulfonyloxymethyl]-6,8-dioxabicyclo[3.2.1]-octane **11***

To a stirred solution of **10** (1.15 g, 3.39 mmol) in CH_2Cl_2 (25 ml) was added ethane dithiol (313 μl, 3.73 mmol) followed by $BF_3 \cdot OEt_2$ (543 μl, 4.41 mmol) at 0°C. After stirring for 3 h at the same temperature, the mixture was treated with H_2O (3 ml) and extracted with Et_2O. The extract was washed with 0.5 N NaOH and brine, dried over $MgSO_4$, evaporated under reduced pressure, and chromatographed (SiO_2, 25 g, elution with Et_2O:hexane=1:5 v/v) to give **11** (1.11 g, 79%) as a colorless oil: $[\alpha]_D^{30}$ +0.48 (*c* 1.10, $CHCl_3$). IR (film): ν=1363, 1176 cm^{-1}. ^1H NMR ($CDCl_3$): δ=7.82 (dt, 2H, *J*=8.5, 1.9 Hz), 7.35 (dd, 2H, *J*=8.5, 0.7 Hz), 4.24 (t, 1H, *J*=6.5 Hz), 4.12 (d, 1H, *J*=1.9 Hz), 3.91 (d, 2H, *J*=6.5 Hz), 3.36–3.17 (m, 4H), 2.45 (s, 3H), 2.25 (ddd, 1H, *J*=14.1, 11.9, 6.0 Hz), 2.07 (ddt, 1H, *J*=14.1, 5.1, 1.9 Hz), 1.86–1.69 (m, 2H), 1.64 (qd, 2H, *J*=7.6, 2.3 Hz), 0.81 (t, 3H, *J*=7.6 Hz). HRMS: calcd for $C_{18}H_{24}O_5S_3$: 416.0786. Found: 416.0775. Anal. calcd for $C_{18}H_{24}O_5S_3$: C 51.90, H 5.81. Found: C 52.04, H 5.72.

*3.9. (1*R,*5*R,*7*S*)-5-Ethyl-7-methyl-2-(1,3-dithiolane)-6,8-dioxabicyclo[3.2.1]octane **12***

A solution of **11** (172 mg, 0.41 mmol) and $LiAlH_4$ (78.4 mg, 2.07 mmol) in THF (5 ml) was refluxed for 8 h. After cooling, the reaction was quenched by addition of water (1 ml) and the mixture was filtered through a Celite pad. The filtrate was evaporated under reduced pressure and chromatographed (SiO_2, 5 g, elution with Et_2O:hexane=1:30 v/v) to give **12** (80 mg, 79%) as a colorless oil: $[\alpha]_D^{29}$ +11.39 (*c* 1.62, $CHCl_3$). ^1H NMR ($CDCl_3$): δ=4.26 (q, 1H, *J*=6.3 Hz), 3.98 (d, 1H, *J*=1.9 Hz), 3.37–3.19 (m, 4H), 2.36 (ddd, 1H, *J*=14.0, 12.0, 5.8 Hz), 2.08 (ddt, 1H, *J*=14.0, 5.2, 1.9 Hz), 1.88–1.64 (m, 4H), 1.24 (d, 3H, *J*=6.3 Hz), 0.96 (t, 3H, *J*=7.6 Hz). HRMS: calcd for $C_{11}H_{18}O_2S_2$: 246.0748. Found: 246.0734.

3.10. (−)-exo-*Isobrevicomin[(1*S,*5*R,*7*S*)-5-ethyl-7-methyl-6,8-dioxabicyclo[3.2.1]octane] **1***

A solution of **12** (62 mg, 0.005 mmol) in EtOH (2 ml) was refluxed with Raney Ni (W-2) (50 mg) for 21 h. After cooling, the mixture was filtered through a Celite pad, evaporated under reduced pressure, and chromatographed (SiO_2, 5 g, elution with Et_2O:pentane=1:20 v/v) to give **1** (22 mg, 56%) as a colorless oil: $[\alpha]_D^{28}$ −55.9 (*c* 1.00, $CHCl_3$) [lit.: $[\alpha]_D^{24}$ −54.3 (*c* 1.34, $CHCl_3$);[1] $[\alpha]_D^{22}$ −60.4 (*c* 1.16, $CHCl_3$)[2]]. ^1H NMR ($CDCl_3$): δ=4.21 (q, 1H, *J*=6.3 Hz), 4.05 (br s, 1H), 1.98–1.43 (m, 6H), 1.18 (d, 3H, *J*=6.3 Hz), 0.96 (t, 3H, *J*=7.4 Hz). The spectral data including ^1H NMR were identical with those reported.[1,2]

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