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Synthesis of (2S,3S)-2,3-Octanediol, the Male Sex Pheromone of the Grape Borer *Xylotrechus Phyrhoderus*

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The grape borer, *Xylotrechus pyrrhoderus*, is known as a major pest of grapevines in Japan and Korea. Recently, Sakai *et al.*¹ isolated the sex pheromone produced by the male grape borer and identified (2S,3S)-2,3-octanediol(**1**) as a major component. Three syntheses of this pheromone have been reported in the literature.¹⁻³ Herein we report an asymmetric synthesis of (-)-**1** starting from readily available 2-deoxy-D-ribose.

Acetonide **2**, prepared⁴ as an anomeric mixture in ~60% yield from commercial (-)-2-deoxy-D-ribose⁵ was condensed with *n*-propylidetriphenylphosphorane in a Wittig reaction, followed by catalytic hydrogenation on Pd/C at atmospheric pressure to provide the saturated alcohol **3**,⁶ $[\alpha]_D^{21} = +30.36^\circ$ ($c = 0.20$, CHCl₃) in 63% overall yield. The alcohol **3** was oxidized with DMSO, oxalyl chloride in the presence of triethylamine to give the aldehyde **4**.⁶ On treatment of **4** with K₂CO₃ in methanol⁷ at room temperature underwent ready epimerization to afford the *trans*-disubstituted dioxolane aldehyde **5** (**5**:**4** = 99.6:0.4⁸). Sodium borohydride reduction of **5** furnished the alcohol **6**,⁶ $[\alpha]_D^{21} = -2.62^\circ$ ($c = 0.20$, CHCl₃) in 83% overall from **3**. Tosylation of **6** followed by reduction with LAH provided the semifinal acetonide **7**.⁶ Hydrolysis of the acetonide **8** with aqueous acetic acid afforded the target

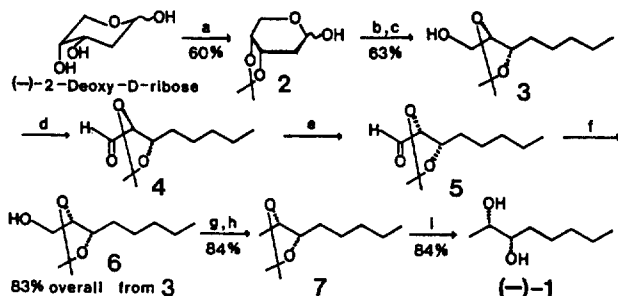
compound (2S,3S)-2,3-octanediol (**1**),^{6,9} $[\alpha]_D^{21} = -18.92^\circ$ ($c = 3.70$, CHCl₃) [lit. $[\alpha]_D^{20} = -18.5^\circ$ ($c = 1.14$, CHCl₃) (Scheme 1)]. The spectral data (¹H-NMR, IR) of (-)-**1** were identical with the data of the synthetic compound provided by Professor K. Mori.

In conclusion, we have synthesized (-)-**1** enantioselectively from (-)-2-deoxy-D-ribose in 22% overall yield.

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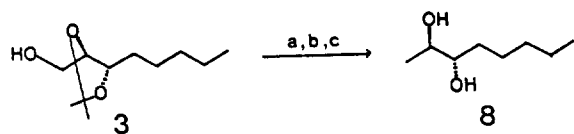
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2. K. Mori and T. Otsuka, *Tetrahedron*, **41**, 553 (1985).
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5. (-)-2-Deoxy-D-ribose is now manufactured by Sam Chul Li Pharm. Co. Ltd., Korea and is available in multigram quantities.
6. Satisfactory spectral and physical data were obtained for the compounds in accord with the structure. Selected physical and spectral data are as follows. (2R,3S)-2,3-Isopropylidenedioxy-1-octanol (**3**): ¹H-NMR (80 MHz, CDCl₃) δ 0.92 (t, 3H), 1.38 (s, 3H), 1.48 (s, 3H), 1.22-1.59 (m, 8H), 3.62 (d, 2H), 4.13 (m, 2H). IR (neat) 3450, 1045 cm⁻¹. $[\alpha]_D^{21} = +30.36^\circ$ ($c = 0.20$, CHCl₃). TLC, SiO₂, R_f = 0.72 (hexanes/ethyl acetate 1:1). (2R,3S)-2,3-Isopropylidenedioxy-1-octanal (**4**): ¹H-NMR (80 MHz, CDCl₃) δ 0.91 (t, 3H), 1.18-1.68 (m, 14H), 4.18 (m, 2H), 9.62 (t, 1H). IR (neat) 2850, 2700, 1720 cm⁻¹. TLC, SiO₂, R_f = 0.49 (hexanes/ethyl acetate 3:1). (2S,3S)-2,3-Isopropylidenedioxy-1-octanol (**6**): ¹H-NMR (80 MHz, CDCl₃) δ 0.90 (t, 3H), 1.36 (s, 3H), 1.50 (s, 3H), 1.18-1.60 (m, 8H), 3.62 (d, 2H), 4.13 (m, 2H). IR (neat) 3400, 1230, 1045 cm⁻¹. $[\alpha]_D^{21} = -2.62^\circ$ ($c = 0.20$, CHCl₃). TLC, SiO₂, R_f = 0.35 (hexanes/ethyl acetate = 3:1). (2S,3S)-2,3-Isopropylidenedioxyoctane (**7**): ¹H-NMR (80 MHz, CDCl₃) δ 0.90 (t, 3H), 1.38 (2S, 6H), 1.18-1.70 (m, 11H), 3.60 (m, 2H). IR (neat) 1240, 1100 cm⁻¹. TLC, SiO₂, R_f = 0.80 (CH₂Cl₂). (2S,3S)-2,3-Octanediol (**1**): ¹H-NMR (80 MHz, CDCl₃) δ 0.90 (t, 3H), 1.10-1.70 (m, 11H), 3.30-3.80 (m, 2H). IR (neat) 3350 cm⁻¹. TLC, SiO₂, R_f = 0.19 (hexanes/ethyl acetate 3:1).
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8. The ratio of the epimers was determined by GLC analysis (Hewlett-Packard 5890GC system) of the reduced alcohols **3** and **6** [column: HP-20M (Carbowax 20M), 0.2 mm \times 25 m, oven temp: 98-150 $^\circ$ C, flow rate: 1.20 kg/cm² (15 psi), carrier gas: N₂, Rt = 5.05 min for **3** and Rt = 4.29 min for **6**].
9. The diastereoisomer **8** was prepared from **3** by tosylation, LAH reduction followed by deprotection.



(a) ref. 4, (b) (C₆H₅)₃P⁺(CH₂)₂CH₃Br⁻, nBuLi, THF, -30 $^\circ$ C \rightarrow rt, 24h, (c) H₂, Pd/C, EtOAc, 1 atm, rt, 36h, (d) DMSO, (COCl)₂, TEA, CH₂Cl₂, -60 $^\circ$ C, 1h, (e) K₂CO₃, MeOH, rt, 4h, (f) NaBH₄, MeOH, rt, 2h, (g) TsCl, pyridine, CH₂Cl₂, 0 $^\circ$ C, 20h, (h) LiAlH₄, ether, reflux, 4h, (i) 50% AcOH, rt, 12h.

Scheme 1



(a) TsCl, pyridine, 0 °C, 20h; (b) LiAlH₄, THF, reflux, 4h;
 (c) 50% HOAc, MeOH, rt, 12h.

The ratio of **1** and **8** in the final product was determined to be 99.4:0.6 by GLC analysis (Hewlett-Packard 5890GC system) [Column, HP-20M (Carbowax 20M), 0.2 mm × 25 m, oven temp: 98–150 °C, flow rate: 1.20 kg/cm² (15 psi), carrier gas: N₂, Rt = 4.55 min for **1** and Rt = 5.20 min for **8**].