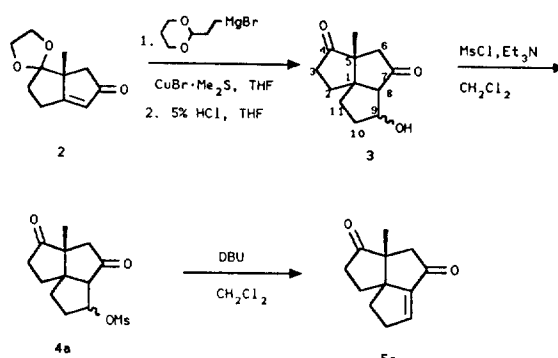
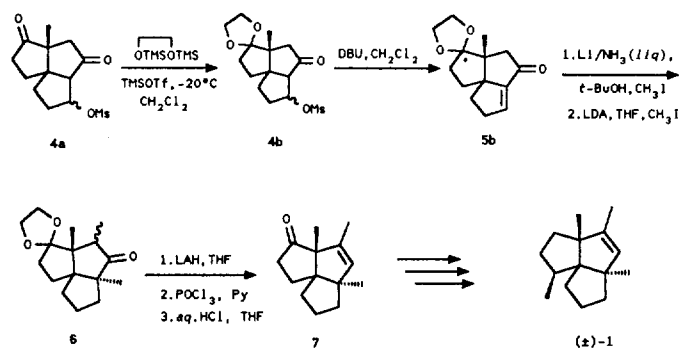


C-6), 4.98, 4.86 (2xd, 2H, $J = 2$ Hz, $=CH_2$), 3.69, 3.41 (ABq, 2H, $J = 18$ Hz, C-2), 1.65 (s, 3H), 1.59 (ds, 3H), 1.39 (s, 9H).

15. Compound 1: IR (KBr): 3200, 1780, 1700, 1380, 1200, 1140 cm^{-1} ; 1H -NMR (300 MHz, DMSO- d_6): δ 9.58 (d, 1H, $J = 9$ Hz, NH), 6.78 (s, 1H), 5.93 (bs, C-7), 5.49 (bs, 2H, $=CH_2$), 5.25 (d, 1H, $J = 5$ Hz, C-6), 3.69 (bs, 2H, C-2), 1.46 (s, 3H), 1.44 (s, 3H).



Scheme 1



Scheme 2

Synthesis of Isocomene Via Selective Monoketalization of Tricyclo[6.3.0.0^{4,8}]-undecadione

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It has been well known that bicyclo[3.3.0]octenones can be utilized as potential intermediates in the synthesis of structurally complicated polyquinanes such as coriolin and gymnomitrol.^{1,2} However, only one example of the construction of tricyclo[6.3.0.0^{4,8}]undecane ring system from bicyclo[3.3.0]octenones has been reported so far.³ We herein describe the construction of tricyclo[6.3.0.0^{4,8}]undecane ring, *i.e.*, isocomene (1) from the monoketal of bicyclo[3.3.0]octenone (2), which was easily prepared from 2-methyl-1,3-cyclopentadione in four steps by analogous method described by Dauben and Hart.⁴

Treatment of 2 with the Grignard reagent derived from 2-(2-bromoethyl)-1,3-dioxane in the presence of the cuprous bromide-dimethyl sulfide complex resulted in smooth 1,4-addition in 92% yield.⁵ Subsequent aldol condensation under acidic condition employing 3% aqueous HCl in refluxing THF for 5 hrs gave a deketalized aldol product 3 in 83% yield. Compound 3 was mesylated with methanesulfonyl chloride in pyridine to obtain 4a in 83% yield and the elimination using DBU provided enone 5a (Scheme 1). But it was necessary to protect the carbonyl group adjacent to the angular methyl in order to introduce methyl group following Birch reduction of the enone 5a. Adopting this strategy, we tried chemoselective monoketalization utilizing conventional method or transketalization,⁶ but we could not obtain the desirable results because of either poor selectivity or decomposition of the product under the reaction conditions.

Therefore, we decided to take on the ketalization prior to the elimination reaction of 4a. Now we could obtain monoketal 4b in 79% yield, which was ketalized at the carbonyl of C-4 adjacent to the angular methyl, by submitting the methanesulfonate derivative 4a to a mild condition of 1,2-bis(trimethylsilyloxy)ether in the presence of TMSOTf at $-20^\circ C$ for 20 hrs in anhydrous dichloromethane.⁷ Perhaps rationale for this selective monoketalization is that bulky methanesulfonate group at C-9 increases the steric crowded-

ness around the carbonyl group at C-7 and this factor facilitates the introduction of ketal at the carbonyl of C-4. Also molecular model of 3 supports this conjecture.

With ketal 4b in our hands, we could smoothly perform the elimination to acquire enone 5b in 89% yield by treating with DBU in anhydrous dichloromethane (Scheme 2). The chemical transformations including Birch methylation and succeeding methylation with LDA and methyl iodide furnished compound 6 in 52% from 5b. The submission of 6 to the reduction with lithium aluminum hydride, the dehydration condition utilizing phosphorus oxychloride and pyridine for 3 days, and deprotection of a ketal group under acidic condition gave eventually the desired product 7^{8,9} in overall yield of 45% from 6. Thus this work constitutes a formal total synthesis of racemic isocomene, because the ketone 7 was already converted to racemic isocomene (1).⁹

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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 pyrhhoderus*, 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

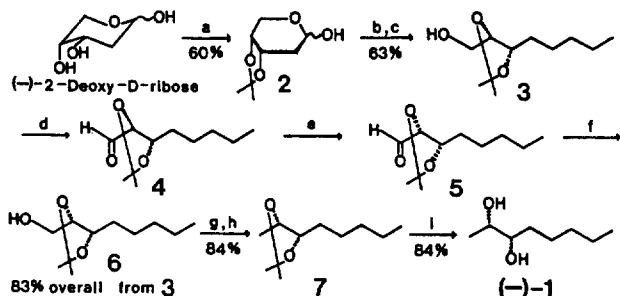
compound (2S,3S)-2,3-octanediol (**1**),^{6,9} $[\alpha]_D^{21} = -18.92^\circ$ ($c = 3.70$, CHCl₃) [lit.² $[\alpha]_D^{20} = -18.5^\circ$ ($c = 1.14$, CHCl₃) (Scheme 1). The spectral data (¹H-NMR, IR) of (-)-**1** were identical with the data of the synthetic compound provided by Professor K. Mori.

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

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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