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-$d_6$): $\delta$ 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).

## Synthesis of Isocomene *Via* Selective Monoketalization of Tricyclo[6.3.0.$0^{4,8}$]-undecadione

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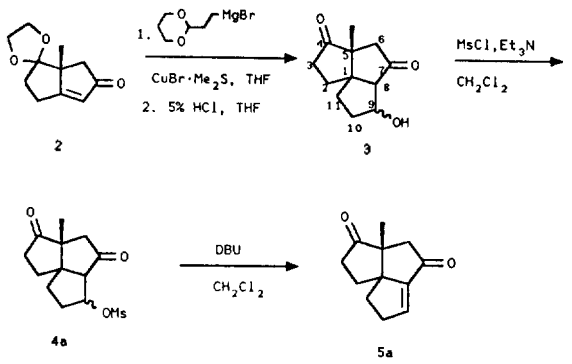
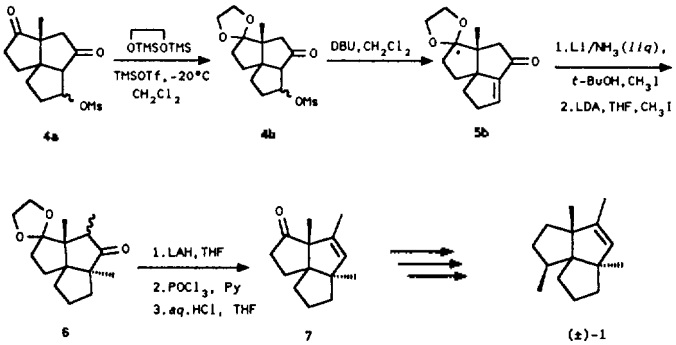
It has been well known that bicyclo[3.3.0]octenones can be utilized as potential intermediates in the synthesis of structurally complicated polyquinanes such as coriolin and gymnomitrol.[1,2] However, only one example of the construction of tricyclo[6.3.0.$0^{4,8}$]undecane ring system from bicyclo[3.3.0]octenones 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 obtaine **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 °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 crowdedness 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.




**Scheme 1**




**Scheme 2**

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]

**Acknowledgement.** We thank Professor Yoon Sup Lee (KAIST) for the support of molecular modeling program.

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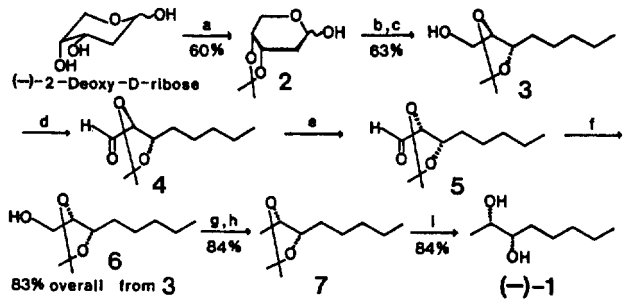
The grape borer, *Xylotrechus pyrrhoderus*, is known as a major pest of grapevines in Japan and Korea. Recently, Sakai *et al.*[1] isolated the sex pheromone produced by the male grape borer and identified (2S,3S)-2,3-octanediol(1) as a major component. Three syntheses of this pheromone have been reported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

Acetonide 2, prepared[4] as an anomeric mixture in~60% yield from commercial (-)-2-deoxy-D-ribose[5] was condensed with *n*-propylidenetriphenylphosphorane 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° (*c* = 0.20, $CHCl_3$) 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 $K_2CO_3$ in methanol[7] at room temperature underwent ready epimerization to afford the *trans*-disubstituted dioxolane aldehyde 5 (5:4 = 99.6:0.4[8]). Sodium borohydride reduction of 5 furnished the alcohol 6,[6] $[\alpha]_D^{21}$ = -2.62° (*c* = 0.20, $CHCl_3$) 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° (*c* = 3.70, $CHCl_3$) [lit.[2] $[\alpha]_D^{20}$ = -18.5° (*c* = 1.14, $CHCl_3$)] (Scheme 1). The spectral data ($^1$H-NMR, IR) of (-)-1 were identical with the data of the synthetic compound provided by Professor K. Mori.




(a) ref. 4, (b) $(C_6H_5)_3P^+(CH_2)_2CH_3Br^-$, nBuLi, THF, -30°C → rt, 24h, (c) $H_2$, Pd/C, EtOAc, 1 atm, rt, 36h, (d) DMSO, $(COCl)_2$, TEA, $CH_2Cl_2$, -60°C, 1h, (e) $K_2CO_3$, MeOH, rt, 4h, (f) $NaBH_4$, MeOH, rt, 2h, (g) TsCl, pyridine, $CH_2Cl_2$, 0°C, 20h, (h) $LiAlH_4$, ether, reflux, 4h, (i) 50% AcOH, rt, 12h.

**Scheme 1**

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

**Acknowledgement.** We gratefully acknowledge financial support from Science and Engineering Foundation. We thank Professor K. Mori for the copies of the spectral data ($^1$H-NMR and IR) for the compound (-)-1.

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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): $^1$H-NMR (80 MHz, $CDCl_3$) 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° (*c* = 0.20, $CHCl_3$). TLC, $SiO_2$, $R_f$ = 0.72 (hexanes/ethyl acetate 1:1). (2R, 3S)-2,3-Isopropylidenedioxy-1-octanal (4): $^1$H-NMR (80 MHz, $CDCl_3$) 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, $SiO_2$, $R_f$ = 0.49 (hexanes/ethyl acetate 3:1). (2S, 3S)-2,3-Isopropylidenedioxy-1-octanol (6): $^1$H-NMR (80 MHz, $CDCl_3$) 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° (*c* = 0.20, $CHCl_3$). TLC, $SiO_2$, $R_f$ = 0.35 (hexanes/ethyl acetate = 3:1). (2S, 3S)-2,3-Isopropylidenedioxyoctane (7): $^1$H-NMR (80 MHz, $CDCl_3$) 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, $SiO_2$, $R_f$ = 0.80 ($CH_2Cl_2$). (2S, 3S)-2,3-Octanediol (1): $^1$H-NMR (80 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.10-1.70 (m, 11H), 3.30-3.80 (m, 2H). IR (neat) 3350 $cm^{-1}$. TLC, $SiO_2$, $R_f$ = 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 × 25 m, oven temp: 98-150°C, flow rate: 1.20 kg/$cm^2$ (15 psi), carrier gas: $N_2$, 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.