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Total Synthesis of (R,Z)-(-)-5-Tetradecen-4-olide, the Pheromone of the Japanese Beetle and Its Biological Activity Test

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Optically active (R,Z)-(-)-5-tetradecen-4-olide, the pheromone of *Popillia japonica* Newman was synthesized from (R)-2,3-O-isopropylideneglyceraldehyde as starting material. The biological activity test of the synthetic pheromone as attractant for the male Japanese beetle was tested in Korea.

Introduction

The Japanese beetle (*Popillia japonica* Newman) is a notorious pest of a variety of trees, ornamentals, and cultivated crops, and the larvae attack the roots of grasses in U.S.A.. In 1977, its pheromone was shown to be (R,Z)-(-)-5-tetradecen-4-olide(1) (Figure 1) by Tumlinson *et al.*[1] Male response was strongly inhibited by small amounts of its (S,Z)-isomer.[1]

Indeed, (R,Z)-1 of 90% optical purity was less than 1/3 as active as the pure pheromone. This fact demands a highly efficient chiral synthesis of (R,Z)-1. The original synthesis of Tumlinson *et al.*[1] involved R(-)-glutamic acid, an unnatural aminoacid as the starting material. Since then, a number of asymmetric synthesis have been reported by resolution[2,3] and by asymmetric reduction[4-6] of an intermediate, an acetylenic keto ester, with varying degree of success. Mori's synthesis[2] depended on the optical resolution of an intermediate and resulted in the synthesis of 1 with 90% optical purity. Pirkle's resolution[3] of his intermediate by HPLC separation was more efficient and yielded 100% optically pure 1. Three groups[4-6] have reported the asymmetric synthesis of (R,Z)-1. The key-step of all of the existing asymmetric syntheses was the reduction of an acetylenic keto ester with a chiral reducing agent[4-6] or with LAH plus a chiral auxiliary.[6] Noyori *et al.*[4] used a binaphthol-modified complex aluminum hydride for the reducing B-3-pinanyl-9-borobicyclo[3.3.1]-nonane, Midland *et al.*[5] (R,Z)-1 in 100% optically pure form, by reduction of acetylenic ketone using LAH and Darvon alcohol or Chirald as a chiral auxiliary and followed by recrystallization. The syntheses via the intermediate by reducing agent were inadequate for a large
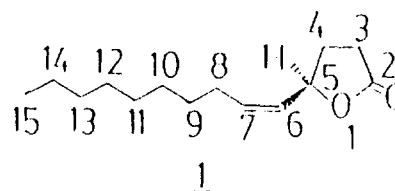

Figure 1

scale preparation. Noyori *et al.*[4] reported the occurrence of some racemization to introduce double bond at C-6 position by the catalytic hydrogenation of the acetylenic ester. scale preparation. Noyori *et al.*[4] reported the occurrence of some racemization to introduce double bond at C-6 position by the catalytic hydrogenation of the acetylenic ester.

Since the pheromone can be used to survey and control this major pest, effective methods for its synthesis would be useful. Here, we wish to report a synthesis of (R,Z)-1 using (R)-2,3-O-isopropylideneglyceraldehyde(5)[7] as starting material.

Results and Discussion

It has been well established that the Wittig olefination reaction when carried out between primary aliphatic aldehyde 3 and saturated aliphatic nonstabilized triphenylphosphonium ylide 2 in a "salt-free" nonpolar condition or in a dipolar aprotic solvent gives (Z)-alkene stereoselectively.[8] A simple retrosynthetic analysis (Scheme 1) reveals that the aldehyde, 5-aldehydo-2-oxotetrahydrofuran(3),[9] the oxidized compound

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of the alcohol, (R)-(-)-5-hydroxymethyl-2-oxotetrahydro-furan(4),[10] is the key intermediate.

We have prepared 5-aldehydo-2- oxotetrahydroturan(3), the key intermediate from (R)-2,3-O-isopropylideneglyceraldehyde and synthesized the pheromone of the Japanese beetle by olefination reaction of 5-aldehydo-2-oxotetrahydroturan(3) with triphenylphosphonium n-nonylide 2.
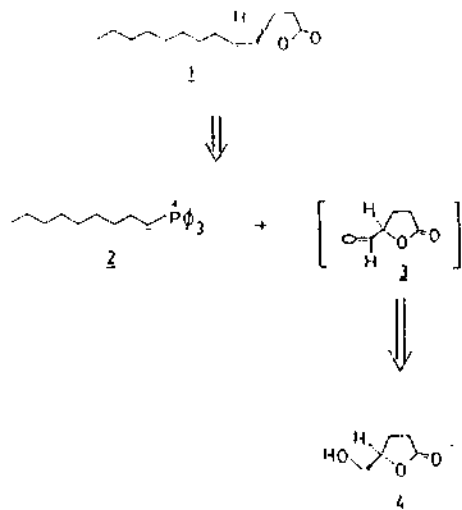
Scheme 1.

Optically active (R)-2,3-O-isopropylidene-D-glyceraldehyde(5)[7] was readily available from naturally abundant and inexpensive D-mannitol. Witting-Emmons olefination[11] of the aldehyde 5 with dimethylmethoxycarbonylmethylenephosphonate furnished the unsaturated ester 6 as a mixture of (E)-:(Z)-=85:15 in 82% yield. Without separation of the mixture, the unsaturated ester 6 was subjected to hydrogenation at atmospheric pressure at room temperature to yield the saturated ester 7 in a good yield. Ester hydrolysis[12] with LiOH in THF-H₂O (3:1) for 3hr followed by deprotection of the acetonide with aqueous AcOH at 75-80°C for 2hr provided (S)-(+)-2-oxotetrahydrofuran 8. The conversion of (S)-(+)-5-hydroxymethyl-2-oxotetrahydrofuran (8)[13] into the required (R)-(-)-5-hydroxymethyl-2-oxotetrahydrofuran (4) was easily performed by the modification of the procedure developed by P-T. Ho.[14] On treatment of the oxotetrafuran alcohol 8 with tosyl chloride at room temperature, a crystalline (S)-tosylate 9 was obtained. Reaction of the (S)-tosylate 9 with lithium benzyloxide in THF gave the (S)-epoxide 10 quantitatively. Exposure of the (S)-epoxide 10 in trifluoroacetic acid at - 10°C resulted in the lactone formation with complete inversion of the configuration to afford (R)-(-)-5-hydroxymethyl-2-oxotetrahydrofuran 4 in overall 83% yield from (S)-hydroxymethyl-2-oxohydrofuran (8). Swern oxidation[15] of the primary alcohol 4 afforded the crude aldehyde 3, the key intermediate. Without further purification, Wittig olefination of the aldehyde 3 with 1.5 equiv. of nonylidenetriphenylphosphonium ylide 2 in tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) at -50°C→rt for 12hr gave the target compound, (R,Z)-(-)-5-tetradecen-4-olide (1);[α]²⁹_D -68.4° (c=5.13, CHCl₃) (lit.,[1] [α]²⁶_D -69.6°) (Scheme 2).
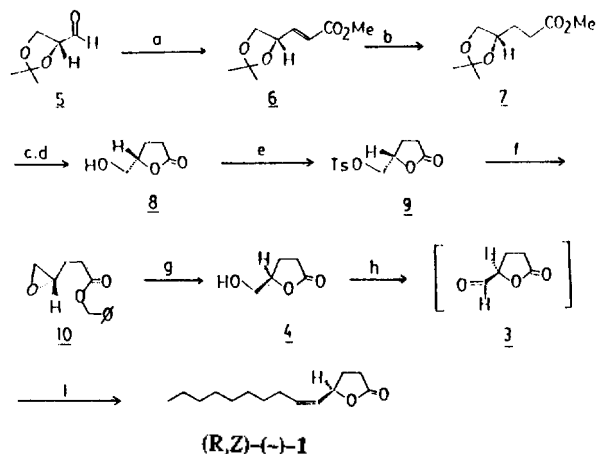
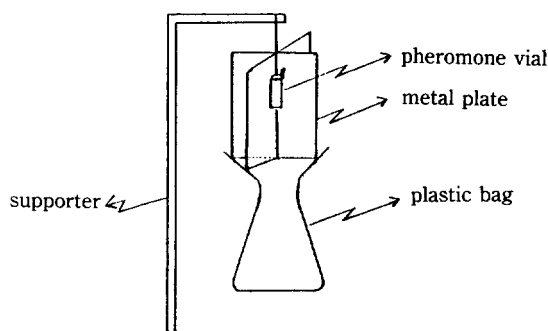**Scheme 2.** Synthesis of (R,Z)-(-)-5-Tetrodecen-4-olide(1).

Figure 2. Schemotic diagram of the trop used.

The synthetic scheme (Scheme 2) above is relatively straightforward and amenable to large scale preparation.

Biological Activity

The biological activity test of the synthetic pheromone as attractant for the male Japanese beetle was conducted in 1986 at the grass field of Livestock Experiment Station in Suwon, Korea. In this experiment, pheromone vials of A and B traps at a concentration of 5 μg and 50 μg per polyethylene capsule were tested from July, 1st to July, 29th, 1986 using the traps baited with the mixtures of (R,Z)-(-)-5-tetradecen-4-olide(1) and (R,E)-(-)-5-tetradecen-4-olide in the ratio of 96:4. The lure materials attached to two metal plates fastened to each other right angles with a funnel-shaped piece at the bottom. The bettles, not noted for their grace and agility, fly along following all the smells until they bang into one of the plates, fall down the funnel into a plastic bag, and are trapped. When the sun shines on the container, it heats up and the beetles

normally die of heat stroke (Figure 2).

Male Japanese beetles captured in the traps biated with (R,Z)-(-)-tetradecen-4-olide containing ca. 4% (R,E)-(-)-isomer were recorded (Table 1). Pheromone vial of the trap A at a concentration of 5 μg could be considered as a blank trap in this case.

Experimental

^{1}H-NMR spectra were taken in chloroform-d, at 80MHz on a BRUKER WP 80 SY spectrometer. Chemical shifts are reported in ppm δ relative to internal tetramethylsilane. Infrared spectra were recorded on a Shimadzu IR-440 spectrophotometer and were calibrated with the 1601 cm^{-1} absorption of polystyrene. Gas chromatograms were obtained on a Varian 3700 gas chromatography. Optical rotations were measured on a JASCO DIP-360 polarimeter. All solvents were distilled before use. Preparative thin layer chromatography (PTLC) was performed by using 20×20cm plates coated with 0.25 or 2 mm thickness of silica gel of GF 254 (Merck). Columm chromatography was performed using Merck silica gel 60 (70–230 mesh). All chromatography solvent were distilled prior to use.

(R)-2,3-O-Isopropylidenglyceraldehyde(5). To a stirred solution of 1,2,5,6-di-O-isopropylidene–D-mannitol (6.85g, 26.2 mmol) in dry CH$_2$Cl$_2$ (80 ml) in an ice bath was added in portions Na$_2$CO$_3$ (27.2g, 0.260 mol) and dry Pb(OAc)$_4$ (12.2g, 27.5 mmol) while maintaining the temperature below 5°C. The reaction mixture was stirred for 30 min with ice cooling and an additional 30 min at room temperature. After filtration through Celite/Na$_2$SO$_4$ with CH$_2$Cl$_2$ (200 ml), the filtrate was concentrated in vacuo. The crude product was distilled on Kugelrohr (39°C, 15mmHg) to afford (R)-2,3-O-isopropylideneglyceraldehyde (5) (5.61g, 81%); IR(NaCl, neat) 2850, 2750, 1725, 1180cm^{-1}; ^{1}H-NMRδ 1.35(3H, s, CH$_3$), 1.46(3H, s, CH$_3$), 4.01–4.18(2H, d, OCH$_2$), 4.24–4.39(1H, m, CH CHO), 9.85(1H, s, CH CHO).

Methyl (4S, 2E)-4,5-isopropylidenedioxypent-2-enoate(6). To a stirred suspension of 50% sodium hydride dispersion (1.01g, 24.2 mmol) (prewashed with dry pentane) in dry dimethoxyethane (60 ml) was added in small portions dimethyl methylcarbonylmethylenephosphonate (4.40g, 24.2 mmol) at room temperature. After the mixture was stirred at room temperature for 1hr under nitrogen, it was treated with (R)-2,3-O-isopropylideneglyceraldehyde (5) (3.15g, 24.2 mmol) in dry dimethoxyethane (6 ml). The reaction mixture

Table 1. The Numbers of Males of the Japanese bettle Captured in the Traps

Date	The numbers of males captured	
	A trap (quantity, 5 μg)	B trap (quantity, 50 μg)
7.1–7.3	1	23
7.4–7.7	1	8
7.8–7.13	0	14
7.14–7.16	0	9
7.17–7.21	0	0
7.22–7.26	0	2
7.27–7.29	1	0

was stirred at 60°C for 1hr, during which time a viscous-semisolid separated. A large excess of water was added, the ether layer was separated, washed with brine and dried over MgSO$_4$, filtered and evaporated to give a residue which was chromatographed on silica gel (50g). Elution with hexane-ethyl acetate (9:1) gave the (E)-olefinic methyl ester 6 (3.96g, 82%) as a syrup; [α]$_D^{20}$ +37.5° (c = 0.29, CHCl$_3$); IR(neat) 1700, 1650cm^{-1}; ^{1}H-NMRδ 1.42(3H, s, CH$_3$), 1.45(3H, s, CH$_3$), 3.63(1H, m, CH CHO), 3.75(3H, s, OCH$_3$), 4.1 (1H, m, OCHHCHO), 4.65(1H, m, CH$_2$CHO), 6.04(1H, dd, J15 and 1.5Hz, CH=CH-CO), and 6.87 (1H, dd, J15 and 6Hz).

Methyl (4S)-4,5-isopropylidenedioxypentanoate(7). To a stirred solution of the olefinic methyl ester 6 (2.80g, 13.8 mmol) in absolute EtOH (40ml) containing 280mg of 10% palladium on charcoal was hydrogenated at 23°C under 1 atm of hydrogen. After the completion of hydrogen absorption (about 4hr), the solution was filtered through Celite and the filtrate was concentrated *in vacuo*. The crude product was distilled on Kugelrohr (67–75°C, 8 mmHg) to afford the saturated ester 7 (2.56g, 92%); IR(neat) 1700, 1650cm^{-1}; ^{1}H-NMRδ 1.42(3H, s, CH$_3$), 1.45(3H, s, CH$_3$), 1.9(2H, m, CH$_2$), 2.5(2H, m, CH$_2$CO$_2$CH$_3$), 3.63(1H, m, CH-O), 3.75(3H, s, OCH$_3$), 4.1(2H, m, CH$_2$-O).

(S)-(+)-5-Hydroxymethyl-2-oxotetrahydrofuran (8). To a stirred solution of the saturated ester 7 (2.20g, 10.9 mmol 1.0 eqiv.) in THF (27 ml)-H$_2$O (9 ml) was added LiOH (344 mg 16.2 mmol 1.5 eqiv.) and the mixture refluxed for 3hr. The resulting mixture was cooled and poured into ice cooled dil. HCl and extracted with ether. The ether layer was washed with brine, dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. Without separation of the mixture, a mixture of the crude pentanoic acid acetonide 7 (1.10g, 6.30 mmol) in aq. AcOH(25 ml) was heated for 2hr between 75 and 80°C. After removing the solvents by azeotropic distillation, the residue was dissolved in benzene and to this mixture was added a catalytic amount of p-TsOH, followed by heating under reflux for 1hr. The mixture was poured into water and extracted with AcOEt. The organic layer was washed with satd. NaHCO$_3$ and brine, and then dried over Na$_2$SO$_4$. After evaporating the solvent, the residue was purified on silica gel (2% methanol in chloroform) to afford the pure lactone 8 (541 mg, 74%); [α]$_D^{20}$ +33.1° (c = 3.17, EtOH); IR(neat) 3400, 1765 cm^{-1}; ^{1}H-NMRδ 2.0–2.8(4H, m, CH$_2$CH$_2$), 3.1 (1H, br, s, OH), 3.5–4.1 (2H, m, CH$_2$O), 4.6(1H, m, -CH-O).

(S)-(+)-5-p-Toluenesulfonyloxymethyl-2-oxotetrahydrofuran(9). To a stirred solution of (S)-(+)-5-hydroxymethyl-2-oxotetrahydrofuran (8) (1.16g, 10 mmol) and tosyl chloride (2.0g) in pyridine (2 ml) and CH$_2$Cl$_2$ (5 ml) was stirred at room temperature for 6hr. The reaction mixture was dissolved in CH$_2$CH$_2$ (40 ml), washed with dil. HCl and dried over MgSO$_4$. After evaporation of the solvent, the product was crystallized from ether/dichloromethane to give the pure tosylate 9 (2.51g, 94%); mp 85-7°C; [α]$_D^{20}$ +46.3° (c = 1.33, CHCl$_3$); IR(KBr, pellet) 1765 cm^{-1}; ^{1}H-NMRδ 1.8–2.7(4H, m, CH$_2$CH$_2$), 2.45(3H, s, CH$_3$), 4.18(2H, d, CH$_2$-O), 4.70(1H, m, CH-O), 7.42(2H, d, J = 10Hz), 7.85(2H, d, J = 10Hz).

Benzyl (S)-(-)-4,5-epoxypentenoate(10). To a stirred solution of benzyl alcohol (1.02 ml, 9.80 mmol) in THF(5 ml) was added a hexane solution of n-BuLi (1.50M, 6.70 ml, 9.80 mmol) at −78°C and the mixture was stirred for 20 min at

-78°C. A solution of the tosylate **9** (2.40g, 8.90 mmol) in THF (20 m*l*) was added at -78°C and the reaction mixture was stirred for 1hr at 0°C. After the addition of satd. NH₄Cl (10 m*l*) and satd. NaCl (10 m*l*), the organic layer was separated and aqueous layer was extracted with benezene (30 m*l* × 2). The combined organic layers were washed successively with water, satd. NaHCO₃, and satd. NaCl, then dried over MgSO₄. The crude product was concentrated *in vacuo* was separated by chromatography (silica gel, benzene : ether/4:1) to afford the epoxy pentenoate **10** (1.60g, 95%) as a colorless oil; $[\alpha]_D^{20}$ - 13.5° (c = 1.1, CHCl₃); IR(neat) 1730, 1160 cm⁻¹; ¹H-NMR*d* 1.66-2.2(2H, m), 2.2-2.9 (4H, m), 2.92 (1H, m), 5.09(2H, s, CH₂Ph), 7.28(5H, s).

(R)-(-)-5-Hydroxymethyl-2-oxotetrahydrofuran (4). A mixture of the epoxide **10** (1.50g, 7.30 mmol) and trifluoroacetic acid (4 m*l*) was stirred at -10°C for 15 min, at which time benzene (50 m*l*) was added and most of the solvent was removed at 35°C using a rotary evaporator. Purification of the residue by chromatography on silica gel eluting with 2% methanol in chloroform gave the pure lactone **4** (731 mg, 86%) as a colorless oil; $[\alpha]_D^{20}$ - 51.4° (c = 5.13, CHCl₃) [lit.,¹⁰ᵃ $[\alpha]_D^{20}$ - 53.5° (c = 3.17, CHCl₃)]; IR, ¹H-NMR spectra were identical in all respects to those of the (S)-(+)- enantiomer **(8).**¹³

(R)-5-Aldehydo-2-oxotetrahydroturan(3). To a solution of CH₂Cl₂(16 m*l*) and oxalyl chloride (0.61 m*l*, 7.0 mmol) was added Me₂SO(1.10 m*l*, 14 mmol) in CH₂Cl₂ (5 m*l*) and the mixture was stirred at -50 to -60°C. The reaction mixture was stirred for 2 min and (R)-(-)-5-hydroxymethyl-2- oxotetrahydrofuran (**4**) (700 mg, 6.03 mmol in 7 m*l* of CH₂Cl₂) was added within 5 min, and stirring was continued for an additional 15 min. Triethylamine (4.2 m*l*, 30 mmol) was added and the reaction mixture was stirred for 5 min and then allowed to warm to room temperature. Water (30 m*l*) was then added and the aqueous layer was reextracted with additional CH₂Cl₂(30 m*l*). The organic layers were combined, washed with satd. NaCl, and dried over MgSO₄. After evaporation the solvent, the crude aldehyde **3**(570 mg) was directly used for the next step without further purification.

(R,Z)-(-)-5-Tetradecen-4-olide(1). A suspension of nonyltriphenylphosphonium bromide (1.36g, 2.90 mmol, 1.5 eqiv.) in dry THF (6.5 m*l*) was stirred until the salt was dissolved at room temperature. The mixture was cooled to -5°C and n-BuLi (1.60 M in hexane, 1.90 m*l*, 2.90 mmol) was added dropwise at such a rate as to keep the temperature below +5°C. After addition of the BuLi, the mixture was held at 0°C for 1hr. The crude aldehyde **3** (231 mg, ca. 1.93 mmol, 1.0 eqiv.) was dissolved in a mixture of dry THF (0.9 m*l*) and HMPA (0.9 m*l*). The aldehyde solvlent mixture was cooled to -50°C and ylide was transferred to the dropping funnel with N₂ and added dropwise to the aldehyde HMPA mixture at or below -35°C until the red color of the ylide persisted in the mixture. The reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was diluted with ice and water and extracted with ether three times. The ether extracts were washed with satd. NaCl and dried over Na₂SO₄. The crude product was chromatographed on silica gel (ether-hexane, 1:9) to afford the pure (R,Z)-(-)-

5-tetradecen-4-olide(**1**) (177mg, 41%). The (R,Z):(R,E) ratio was 96:4 by gas chromatography on carbowax 20M; $[\alpha]_D^{20}$ - 68.4° (c = 5.13, CHCl₃) (lit.,¹ $[\alpha]_D^{25}$ - 69.6°); IR(neat) 3020, 2940, 1790 cm⁻¹; ¹H-NMR*d* 0.88 (3H, t, CH₃), 1.0-1.5(12H, br.s, -(CH₂)₆-), 1.5-2.5(6H, m, CH₂-CH=CH, -CH₂CH₂-), 5.06(1H, m, CH₂CHO), 5.20-5.68(2H, m, -CH=CH-).

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