

## 벼의 이화명충의 성유인물질인 (Z)-13-옥타데센-1-알의 합성

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## Synthesis of (Z)-13-Octadecen-1-al, a Pheromone Component of the Rice Stem Borer, *Chilo suppressalis*

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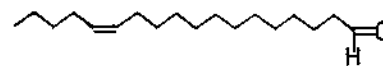
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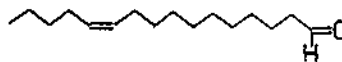
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(Z)-13-Octadecen-1-al (1) and (Z)-11-hexadecen-1-al (2) (Fig. 1) were isolated<sup>1</sup> in the ratio of approximately 1 : 4.5 as the pheromone complex of the rice stem borer, *Chilo suppressalis*, a serious pest of rice in Asian countries<sup>2</sup>. Field test on mating confusion of the synthetic pheromone in Korea has been already carried out<sup>3</sup>. The two components of the pheromone were synthesized by the conventional acetylenic route<sup>4</sup>. In 1979, Bestmann *et al.*<sup>5</sup> reported a synthesis of (Z)-13-octadecen-1-al by Wittig olefination of methyl 13-oxotridecanoate with pentylidenetriphenylphosphonium ylide and the subsequent conversion of the resulting methyl (Z)-13-octadecenoate into the (Z)-13-octadecen-1-al. Methyl 13-oxotridecanoate was prepared from methyl brassidate or erucate by ozone cleavage reaction. After ozonolysis of the methyl brassidate or erucate and reduction with triphenyl phosphine, the two aldehydes thus formed were separated.

We worked out a Wittig route to (Z)-13-octadecen-1-al, starting from readily available 1,12-dodecandicarboxylic acid (Scheme 1). Esterification (MeOH/H<sup>+</sup>) of the 1,12-dodecandicarboxylic acid, followed by partial hydrolysis (MeOH/KOH) of the resulting diester gave 1,12-dicarboxylic acid monomethylester (3) in 83% yield. The monomethylester (3) was converted to bromoester (4) by the Cristol-Firth modification<sup>6</sup> (Br<sub>2</sub>/HgO, 81%) of the Hunsdiecker reaction. Heating the bromoester (4) at reflux with pyridine-N-oxide and sodium bicarbonate

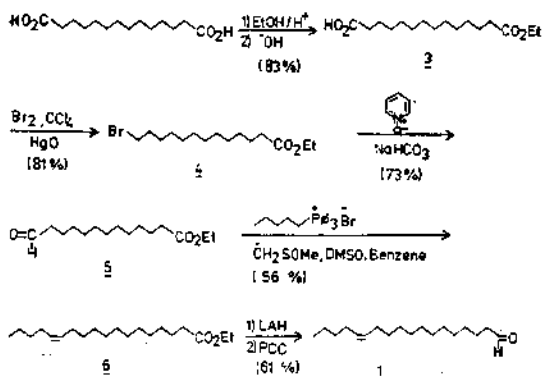


1



2

Fig. 1.



Scheme 1.

in toluene under nitrogen atmosphere<sup>7</sup> yielded methyl 13-oxotridecanoate(5) in 73% yield. The methyl (Z)-13-octadecenoate(6) was obtained in 56% yield by olefination of the methyl 13-oxotridecanoate(5) with pentylidenetriphenylphosphonium ylide generated in situ by dimsyl anion<sup>8</sup> in DMSO and benzene. Lithium aluminum hydride reduction of the olefin ester (6), followed by PCC oxidation<sup>9</sup> afforded (Z)-13-octadecen-1-ol in 61% yield.

### EXPERIMENTAL

Infrared spectra were recorded with Shimadzu IR-440 Spectrophotometer. Proton NMR were taken on a BRUKER WP 80 SY 80MHz NMR Spectrophotometer, using tetramethylsilane as an internal reference. All solvents and liquids were distilled before use.

**1,12-Dodecanedicarboxylic acid monomethyl ester(3).** To a solution of 1,12-dodecanedicarboxylic acid(1.05g) in methanol(17ml) was added concentrated sulfuric acid(0.62ml). The reaction mixture was heated at reflux for 2hr. After the reaction mixture has been diluted with 3 volumes of water, extracted with benzene. The benzene extracts was washed successively with water, 5% aqueous sodium carbonate solution, and water. The organic layer was dried over anhydrous magnesium sulfate and concen-

trated in vacuo to give 1,12-dodecanedicarboxylic acid dimethylester, a white solid(1.17g, 99%; m.p. 34°C). IR  $\text{cm}^{-1}$ : Peak of O-H stretching vibration was disappeared.

To a solution of 1,12-dodecanedicarboxylic acid dimethylester (1.11g) in dry methanol (1.72ml) was added a solution of potassium hydroxide(0.21g) in dry methanol(1.72ml) at room temperature during a period of 1hr. White crystalline precipitate formed during the addition, and after all the hydroxide has been added, stirring was continued for an additional 2hr. After the reaction mixture has stood overnight with stirring, the solid was collected by suction filtration, washed with a small amount of ether, and dried under reduced pressure at room temperature. The solid(1.25g) was charged with water (4.30ml), cooled to 5°C in an ice bath, and added concentrated hydrochloric acid(0.34 ml) over a 15min period. The reaction mixture was stirred at 5°C for 10min. The organic layer was extracted with ether, washed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 1,12-dodecanedicarboxylic acid monomethylester(3) (0.88g, 83%). m.p. 80~85°C. IR  $\text{cm}^{-1}$ : 3500~3000, 2900, 2850, 1725, 1700, 1460, 1430, 1260, 1160, 880, NMR  $\delta$ : 1.20~1.80(m, 20H), 2.35(m, 4H), 3.65(s, 3H).

**Methyl 13-bromotridecanoate(4).** To a solution of red mercuric oxide(1.02g) in carbon tetrachloride(8.50ml) was added monomethylester(3) (0.70g), and heated to reflux for 2hr (the reaction flask was wrapped with aluminum foil to exclude light). After the reaction mixture was cooled at room temperature, bromine (0.20ml) in carbon tetrachloride(3ml) was added slowly. The reaction mixture was heated at reflux and stirred for 2hr, and then filtered. The filtrate was washed with water, 5~10% nitric acid solution, and again water. The

organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to give methyl 13-bromotridecanoate (4) (0.64g, 81%). IR  $\text{cm}^{-1}$ : 2920, 2850, 1730, 1450, 1430, 1250, 1020, 780, NMR  $\delta$ : 1.10~2.10(m, 20H), 2.16 (t, 2H), 3.45(t, 2H), 3.70(s, 3H).

**Methyl 13-oxotridecanoate(5).** To a solution of methyl 13-bromotridecanoate(4) (0.52g) in toluene (8ml) was added pyridine-N-Oxide (0.33g) and sodium bicarbonate(0.30g) under nitrogen atmosphere. The reaction mixture was heated at 110°C for 4hr. After cooling, to the reaction mixture was added sodium bicarbonate (0.30g), and stirred at 110°C for 4hr. The reaction mixture was cooled to room temperature and poured into ice water(8.0ml). Toluene was evaporated, the residue was extracted with petroleum ether, washed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give methyl 13-oxotridecanoate(5) (0.28g, 73%). IR  $\text{cm}^{-1}$ : 2920, 2850, 2730, 1725~1715, 1450, 1250, 1020, 720. NMR  $\delta$ : 0.80~1.80(m, 18H), 2.35(br. t, 4H), 3.70(s, 3H), 9.75(t, 1H).

**Methyl (Z)-13-octadecenoate(6).** The solution of sodium hydride(0.09g) in dimethyl sulfoxide(6.0ml) was heated at 50°C for 1hr under nitrogen atmosphere, and then cooled to room temperature. To this solution, was added pentyltriphenylphosphonium bromide(1.72g) in DMSO(3.0ml). To the pentylidenetriphenylphosphonium ylide thus formed was added methyl 13-oxotridecanoate(5) (0.20g) in DMSO (2.0ml), stirred for 2hr, and diluted with dry benzene(8.0ml). The reaction mixture was stirred at room temperature for 3hr, added water (20ml), and extracted with ether: n-hexane (1:1). The ether-hexane layer was separated, washed with water, dried over anhydrous magnesium sulfate, concentrated in vacuo, and separated by flash column chromatography using

ether: petroleum ether(1:1) as eluent to give methyl (Z)-13-octadecenoate (6) (0.14g, 56%). IR  $\text{cm}^{-1}$ : 2920, 1730, 1460, 1230, 1050. NMR  $\delta$ : 1.00~1.90(m, 29H), 2.15(t, 2H), 3.65(s, 3H), 5.40(t, 2H, J=5Hz).

**(Z)-13-Octadecen-1-al(1).** To a solution of lithium aluminum hydride(0.01g) in dry ether (1.0ml) was added dropwise methyl 13-octadecenoate(6) (0.12g) in dry ether(1.0ml) at room temperature. The reaction mixture was heated at reflux for 1hr. After cooling, 6N-hydrochloric acid solution(1.0ml) was added and extracted with ether, washed with water, dried over anhydrous magnesium sulfate, concentrated in vacuo to give (Z)-13-octadecene-1-ol(0.10g, 93%).

To a stirred solution of pyridinium chlorochromate(0.08g) in dry dichloromethane(2.0ml) was added in one portion (Z)-13-octadecen-1-ol (0.07g) in dry dichloromethane(2ml). The reaction mixture was stirred at room temperature for 2hr. The reaction mixture was dissolved in ether and washed thoroughly from the black gum. Ether and dry dichloromethane were evaporated and the residue was extracted with ether, washed with saturated sodium bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate, concentrated in vacuo, and purified by column chromatography using cyclohexane: ethyl acetate(1:2) as eluent to afford (Z)-13-octadecen-1-al (1) (0.07, 66%), IR  $\text{cm}^{-1}$ : 2920, 2710, 1725, 1460. NMR  $\delta$ : 1.0~1.8(m, 29H), 2.45(t, 2H), 5.40(m, 2H, J=5Hz), 9.80(t, 1H, J=2Hz).

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