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### A New Synthesis of (E,E)-8, 10-Dodecadien-1-ol, Sex Pheromone of Codling Moth

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Note

A New Synthesis of (E,E)-8,10-Dodecadien-1-ol, Sex Pheromone of Codling Moth\*

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JMS-D300 spectrometer at 22 eV.

(E,E,)-2,4-Hexadienyl bromide (sorbyl bromide). The compound was prepared by treating sorbyl alcohol with triphenylphosphine dibromide in methylene chloride.

Ethyl 2-[(E,E,)-2,4-hexadienyl]-3-oxoglutarate (2). To a solution of magnesium ethoxide prepared freshly from magnesium turnings (7.2 g, 0.3 mol) and iodine in absolute alcohol (270 ml), ethyl 3-oxoglutarate (1, 40.4 g, 0.2 mol) was added dropwise over a period of 0.5 hr with stirring and the solution was refluxed for 1 hr. The solution was then allowed to cool to room temperature, sorbyl bromide

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(*E,E*)-8,10-Dodecadien-1-ol (5) is the sex pheromone of the codling moth, *Laspeyresia pomonella*, which is a serious pest in apple orchards.<sup>1,2)</sup>

For the synthesis of physiologically active substances we are investigating the use of the selective alkylation of ethyl 3-oxoglutarate (1) and have previously reported the syntheses of (Z)-jasmone and methyl jasmonate,<sup>3</sup> which are the main principles of the characteristic jasmine fragrance, and 2-(6-methoxycarbonylhexyl)cyclopent-2-en-1-one,<sup>4</sup> which is a valuable intermediate in prostaglandin syntheses. The present paper deals with a new approach applying the selective alkylation of the ester 1 to the synthesis of the sex pheromone 5.

Alkylation of ethyl 3-oxoglutarate (1) with sorbyl bromide (E,E-conjugated diene) in the presence of magnesium (35.4 g, 0.22 mol) was added over 1 hr at a constant rate and the mixture was refluxed for 18 hr with stirring. After the solvent in the reaction mixture was distilled off *in vacuo*, the residue was acidified with 10% HCl and extracted with ether. The ether solution was washed with a 5% aqueous solution of NaHCO<sub>3</sub>, water and brine in succession, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated *in vacuo* to give the compound 2 as a dark brown viscous liquid, which was purified as a yellow viscous liquid (40 g, 71%) by silica gel (Merck Kieselgel 60) column chromatography with a *n*hexane-ether (10:1) mixed solvent. IR  $v_{max}$  cm<sup>-1</sup>: 3020, 1730, 1710, 1025, 985. NMR  $\delta$  (CDCl<sub>3</sub>): 1.25 (6H, t, J=7.5 Hz), 1.70 (3H, d, J=6.0 Hz), 2.58 (2H, t, J=6.8 Hz), 3.55 (2H, s), 3.68 (1H, t, J=6.8 Hz), 4.18 (4H, q, J=7.5 Hz), 5.05~6.15 (4H, m).

Methyl 5-oxo-(E,E)-8,10-dodecadienoate (3). A solution of 2 (56.4 g, 0.2 mol) in dry 1,2-dimethoxyethane (DME, 50 ml) was added dropwise to a stirred solution of sodium hydride (9.6 g of a 50% mineral oil dispersion, 0.2 mol) in

ethoxide gave 2-[(*E*,*E*)-2,4-hexadienyl]-3-oxoglutarate (2) with a yield of 71%. By the treatment of 2 with sodium hydride as the base and subsequently with ethyl 3-bromopropionate in 1,2-dimethoxyethane, followed by decarboxylative hydrolysis with an aqueous solution of sodium hydroxide, the corresponding keto acid was obtained, which afforded a methyl ester (3) with a ~46% yield from 2. The keto ester 3 via tosylhydrazone was reductively deoxygenated by heating with sodium cyanoborohydride in acidic dimethylformamide-sulfolane<sup>5</sup> to give an ester (4), which was finally reduced to the desired alcohol  $5^{2.6}$  with lithium aluminum hydride (38% yield from 3).

## EXPERIMENTAL PROCEDURES

All boiling points and melting points were uncorrected. IR spectra were determined with films with a Hitachi 260-10 spectrometer. NMR spectra were recorded with a Hitachi R-24B instrument at 60 MHz using TMS as an internal standard. GC-MS was performed with a JEOL

dry DME (150 ml) at room temperature and stirring was continued for 1 hr. Ethyl 3-bromopropionate (43.4 g, 0.24 mol) and finely powdered sodium iodide (8g) were then added to the solution and the mixture was refluxed for 18 hr with stirring. The reaction mixture was cooled to room temperature, and the solvent was distilled off in vacuo. The residue was heated with a 15% aqueous solution of NaOH (500 ml) under reflux for 20 hr, and the reaction mixture was acidified with conc. HCl, saturated with NaCl and extracted with ether. The ether solution, after being washed with brine and dried over  $Na_2SO_4$ , was evaporated in vacuo. The crude keto acid thus obtained was subjected to esterification with a mixture of methanol (20 ml), 1,2dichloroethane (150 ml) and conc.  $H_2SO_4$  (3 ml). The reaction mixture was worked up by the usual procedure to give 3 as a yellow liquid, bp  $105 \sim 120^{\circ}C$  (0.4 mmHg), silica gel (Merck Kieselgel 60) column chromatography of which with *n*-hexane-ether (8:1) gave the methyl ester 3 (20.6 g, 46%) in an analytically homogeneous state, bp  $110 \sim 112^{\circ}C$ (0.25 mmHg). IR  $v_{max}$  cm<sup>-1</sup>: 3020, 1735, 1710, 1630, 990.

## NMR $\delta$ (CCl<sub>4</sub>): 1.70 (3H, d, J = 6.0 Hz), 1.85 ~ 2.50 (10H,

m), 3.58 (3H, s),  $5.10 \sim 6.38 (4H, m)$ . MS m/e: 224 (M<sup>+</sup>, 24),

# \* Selective Alkylation of Ethyl 3-Oxoglutarate. Part 192 ( $M^+$ -CH<sub>3</sub>OH, 100), 129 (87), 101 (62), 81 (79), 59 (14). IV. For part III, see ref. 3.

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(1)

 $\underbrace{\overset{i}{\underset{EtO_2C}{(2)}} \overset{i}{\underset{CO_2Et}{(3)}} \underbrace{CO_2Et}{(3)}$ 





Methyl (E,E)-8,10-dodecadienoate (4). To a mixed solution of 3 (15.7 g, 0.07 mol) and p-toluenesulfonylhydrazine (16.3 g, 0.0875 mol) in DMFsulfolane (350 ml, 1:1) was added p-toluenesulfonic acid (1.75 g) and sodium cyanoborohydride (17.6 g, 0.28 mol) at room temperature, and the solution was heated at  $100^{\circ}C$ for 4 hr. After cooling to room temperature, the reaction mixture was diluted with water (1000 ml) and extracted with cyclohexane. The cyclohexane solution was washed with water, dried over  $Na_2SO_4$  and concentrated in vacuo. Column chromatography of the oily residue over silica gel (Merck Kieselgel 60) with petroleum ether-ether (10:1) gave 4 (5.6 g, 38%) as a pale yellow liquid, bp  $107 \sim 110^{\circ}$ C (0.4 mmHg). IR  $v_{max}$  cm<sup>-1</sup>: 3020, 1735, 1630, 985. NMR  $\delta$  $(CCl_{4})$ : 1.35 (8H, m), 1.74 (3H, d, J = 6.0 Hz), 1.90 ~ 2.45 (4H, m), 3.62 (3H, s),  $5.30 \sim 6.25$  (4H, m). MS m/e: 210  $(M^+, 100), 178 (M^+-CH_3OH, 46), 82 (28), 81 (45), 68 (62).$ 

up by the usual procedure to give the alcohol 5, with a nearly quantitative yield, which solidified during storage in a refrigerator, mp  $28 \sim 29^{\circ}$ C (recrystallized from petroleum ether). The purity was 97% on GLC analysis (10%) SE-30, 2 m, at 100 ~ 220°C, 8°C/min). IR  $v_{max}$  cm<sup>-1</sup>: 3340, 3020, 1630, 985. NMR  $\delta$  (CDCl<sub>3</sub>): 1.74 (3H, d, J = 6.0 Hz), 3.58 (2H, t, J = 7.0 Hz),  $5.25 \sim 6.32$  (4H, m). MS m/e: 182  $(M^+, 90).$ 

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(E,E)-8,10-Dodecadien-1-ol (5). A solution of 4 (4.2 g, 0.02 mol) in absolute ether (40 ml) was added dropwise to a slurry of lithium aluminum hydride (0.38 g, 0.01 mol) in absolute ether (60 ml) with stirring at room temperature. Stirring was continued for 1 hr at room temperature. After the mixture was refluxed for 1 hr, the reaction was quenched with  $2 \times H_2SO_4$  (30 ml) and the mixture was worked

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