INSECT PHEROMONES AND THEIR ANALOGS.
XI. SYNTHESIS OF 2,6-DIMETHYLHEPTA-1,6-DIEN-3-OL ACETATE – THE SEX ATTRACTANT OF *Pseudococcus comstocki*

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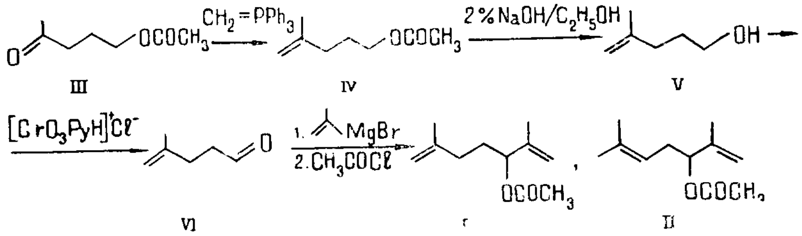
A new synthesis of 2,6-dimethylhepta-1,6-dien-3-ol acetate (I) – the sex attractant of The Comstock mealybug – has been developed.

2,6-Dimethylhepta-1,6-dien-3-ol acetate (I) – the probable biogenetic precursor of the sex pheromone of the Comstock mealybug, *Pseudococcus comstocki* Kuwana – has half the activity of the natural pheromone – 2,6-dimethylhepta-1,5-dien-3-ol (II) – and has been synthesized recently from isopulegol [2] and from methyl heptenone [3] with yields of 17, and 10%, respectively. We have developed a new route to the synthesis of the attractant (I) from the readily available 5-acetoxypentan-2-one (III) with an overall yield of 30%.



The olefination of the acetoxyketone (III) with methylenetriphenylphosphorane, obtained from methyltriphenylphosphonium bromide and potassium tert-butanolate in THF, gave a 60% yield of 4-methylpent-4-enol acetate (IV), the hydrolysis of which led in high yield to 4-methylpent-4-enol (V). Under the action of pyridinium chlorochromate in methylene chloride the alcohol (V) was converted with 70% yield into 4-methylpent-4-enal (VI), the condensation of which, with isopropenylmagnesium bromide and acetylation of the intermediate magnesium alcoholate with the aid of acetyl chloride, led to the desired dienic acetate (I).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (with the substances in the form of films). PMR spectra of solutions of the substances in CDCl$_3$ were measured relative to TMS on a Tesla BS-487B instrument (80 MHz). GLC analysis was carried out on a Chrom-4 instrument with SE-30 (5%) on Chromaton N-AW-DMCS (0.2-0.25 mm) as the stationary phase at a working temperature of 50-150°C (14 deg/min) with helium as the carrier gas.

4-Methylpent-4-enol Acetate (IV). A suspension of 64 g (180 mmole) of methyltriphenylphosphonium bromide in 600 ml of absolute THF was treated at –30°C with 20 g (180 mmole) of potassium tert-butanolate in 60 ml of absolute THF (Ar), the mixture was stirred for 30 min, and a solution of 17.3 g (120 mmole) of the keto acetate (III) in 60 ml of absolute THF was added dropwise. The reaction mixture was kept at –30°C for 1 h and was then gradually warmed to room temperature and was left for 16 h, after which 1000 ml of pentane was added and it was filtered. The filtrate was washed with a saturated solution of NaCl and was dried with MgSO$_4$. The residue after evaporation was chromatographed [SiO$_2$, hexane–ether (1:1)], which led to to isolation of 10 g (60%) of the acetate (IV), R$_f$ 0.8. IR spectrum (ν, cm^{-1}): 890 s, 1050 s, 1180 s, 1250 s, 1370 s, 1440 s, 1655 m, 1740 s, 3080 m. PMR spectrum (δ, ppm): m

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1.23 (2 H, CH_2); s 1.65 (3 H, CH_3—C=C); m 1.92 (2 H, CH_2C=C); s 1.93 (3 H, CH_3C=O); t 3.98 (2 H, CH_2O, J = 6 Hz); s 4.65 (2 H, CH_2=C).

4-Methylpent-4-enol (V). A mixture of 9 g of the acetate (IV) and 250 ml of 2% NaOH in 250 ml of ethanol was stirred at room temperature for 5 h and was then left for 16 h, after which 40 g of dry NaCl and 600 ml of diethyl ether were added and the mixture was stirred for another 1 h. The organic fraction was separated off and was washed twice with NaCl solution and dried with $MgSO_4$. After evarporation, 5.4 g (85%) of the alcohol (V) was obtained with n_D^{20} 1.4375 [4]. IR spectrum (ν, cm^{-1}): 890 s, 1380 s, 1470 s, 1655 m, 3080 m, 3400 br.s. PMR spectrum (δ, ppm): m 1.42-1.75 (2 H, CH_2); s 1.65 (3 H, CH_3); m 1.79-2.15 (2 H, CH_2C=C); t 3.48 (2 H, CH_2—O, J = 6 Hz); br.s. 4.08 (1 H, OH); s 4.6 (2 H, CH_2=C).

4-Methylpent-4-enal (VI). With stirring, 4.4 g (44 mmole) of 4-methylpent-4-enol (V) was rapidly added to a suspension of 14.25 g (66 mmole) of pyridinium chlorochromate obtained by the method of Corey and Suggs [5] in 20 ml of dry methylene chloride. The mixture was stirred at room temperature for 1 h and then 25 ml of absolute diethyl ether was added and, after 30 min, the solution was decanted off and the solid residue was extracted with ether (4 × 5 ml). The combined solution was filtered through a layer of silica gel (5 g) on a Schott funnel. The solvent was evaporated off and the residue was distilled in vacuum. This gave 3 g of the aldehyde (VI) (70%), with bp 43-45°C/45 mm Hg [6]. IR spectrum (ν, cm^{-}): 900 s, 1050 m, 1080 m, 1130 m, 1300 w, 1380 m, 1390 m, 1420 m, 1450 s, 1655 m, 1730 s, 2745 m, 3080 m. PMR spectrum (δ, ppm): br.s. 1.73 (3 H, CH_3); m 2.4 (4 H, CH_2); br.s. 4.63 (2 H, CH_2=C); s 9.68 (1 H, CH=O).

2,6,-Dimethylhepta-1,6-dien-3-ol Acetate (I). A suspension of 0.8 g (34 mmole) of Mg in 30 ml of absolute THF was treated with a small crystal of iodine and was then heated to 40-45°C, and 3.86 g (32 mmole) of isopropenyl bromide was added. The reaction mixture was kept at room temperature for 1 h and was then cooled to 0°C, and, with vigorous stirring, a solution of 2.95 g (30mmole) of the aldehyde (VI) in 5 ml of absolute THF was added. The mixture was warmed to room temperature and was kept for 30 min, after which it was cooled to 0°C and treated with 3.25 ml (45 mmole) of acetyl chloride and was then again warmed to room temperature and was kept for 30 min. The reaction mixture was decomposed by the addition of 20 ml of a saturated solution of NH_4Cl at 0°C, after which 40 ml of ether was added and the whole was stirred for 1 h. The organic layer was separated off and was washed with a 5% solution of $NaHCO_3$ (2 × 10 ml) and then with saturated NaCl solution (3 × 10 ml) and was dried with Na_2SO_4 and evaporated. Vacuum distillation of the residue (4.4 g) yielded 4.1 g (75%) of the acetate (I) with bp 54°C/2 mm Hg n_D^{20} 1.4474 [2].

IR spectrum (ν, cm^{-1}): 900 m, 1030, s, 1060 m, 1250 s, 1380 m, 1450 m, 1655 m. 1745 s, 3085 m. PMR spectrum (CCl_4, δ, ppm): br.s. 1.7 (6 H, CH_3C=C); m 1.92 (4 H, CH_2); s 1.93 (3 H, CH_3C=O); br.s. 4.63 (2 H CH_2=C); br.s. 4.8 and br.s. 4.87 (2 H, CH_2=C);t 5.05 (1 H, CHO, J = 6 Hz).

SUMMARY

A new route for the synthesis of 2,6-dimethylhepta-1,6-dien-3-ol- acetate — an attractant of the Comstocks mealybug — has been developed on the basis of the readily accessible 5-acetoxypentan-2-one.

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