

SYNTHESIS OF QUEEN BEE PHROMONE

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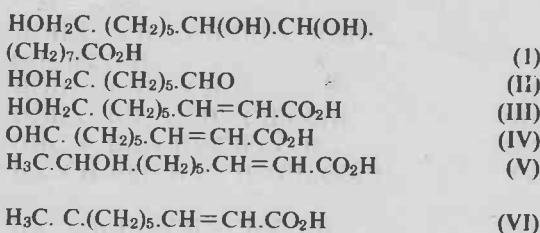
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THE mandibular glands of the queen honey-bee, *Apis mellifera*, secrete the queen substance which principally contains 9-oxo- Δ^2 -decanoic acid. The queen substance inhibits the development of ovaries and prevents queen rearing in workers. It also acts as sex attractant in mating¹.

9-oxo- Δ^2 -decanoic acid (VI) has been synthesised from a number of starting materials²⁻¹⁰. We report here its synthesis from 7-hydroxyheptanal, one of the periodate oxidation products of aleuritic acid, the major constituent acid of shellac.

7-Hydroxyheptanal (II), on condensation with malonic acid in the presence of pyridine gave an α , β -unsaturated hydroxy acid (III), which on oxidation with pyridiniumchlorochromate resulted in an unsaturated aldehydic acid (IV).

The carbinol (V) obtained by the condensation of IV with CH_3MgI on further oxidation with aluminium tert. butoxide yielded 9-oxo- Δ^2 -decanoic acid (VI).



7-Hydroxyheptanal (II)

Threo-aleuritic acid (I, m.p. 99-100°, 8 g) in methanol-water (400 ml, 1:1) at 40°C on sodium periodate oxidation¹¹ for 10 min and on usual workup afforded 7-hydroxyheptanal as liquid (3.2 g). It was purified through a column of neutral alumina by eluting with ether. I.R.(Neat): 3250, 1720 cm^{-1} (Found: C, 64.80; H, 10.72. Calcd. for: $\text{C}_7\text{H}_{14}\text{O}_2$: C, 64.70; H, 10.80%).

9-Hydroxy- Δ^2 -nonenoic acid (III)

The above hydroxyaldehyde (II, 3 g) was heated on a steam bath for 4 hr with malonic acid (3 g) in dry pyridine (5 ml). Extraction with ether yielded the unsaturated hydroxy acid as thick liquid (2.8 g), which was purified over a column of neutral alumina in ether. I.R.(Neat): 3250, 1700, 970 cm^{-1} (Found: C, 62.72; H, 9.24. Calcd. for $\text{C}_9\text{H}_{16}\text{O}_3$: C, 62.80; H, 9.30%).

 Δ^2 -Noneldehydic acid (IV)

A solution of III (2 g) in dry methylene chloride (10 ml) was added with stirring to a suspension of pyridinium chlorochromate (3.28 g) and anhydrous sodium acetate (0.25 g) in dry methylene chloride. After 2 hr, dry ether was added and the supernatant decanted from the black gummy mass. The ethereal extract was then passed through a column of neutral alumina to remove the impurities and the solvent was evaporated off to obtain IV (1.4 g) as thick oil. I.R.(Neat): 1725, 1700, 970 cm^{-1} (Found: C, 63.50; H, 8.20. $\text{C}_9\text{H}_{14}\text{O}_3$ requires C, 63.52; H, 8.23%).

9-Hydroxy- Δ^2 -decanoic acid (V)¹²

The above compound (IV, 2.5 g) in dry ether (10 ml) was condensed with CH_3MgI . The resultant product (V) obtained as liquid (2 g) was purified through a column of neutral alumina in ether. I.R.(Neat): 3250, 1700, 970 cm^{-1} . (Found: C, 64.42; H, 9.63. $\text{C}_{10}\text{H}_{18}\text{O}_3$ requires C, 64.51; H, 9.70%).

9-oxo- Δ^2 -decanoic acid (IV)

The above carbinol (2 g) in a mixture of dry acetone (15 ml) and benzene (20 ml) was heated at 80° for 8 hr with a solution of aluminium tert. butoxide (3.4 g in dry benzene). It was then cooled and treated with 10% H_2SO_4 (10 ml). On workup with benzene, VI was obtained as solid (1.2 g) and was crystallised from methanol m.p. 53-55° (lit.⁷, 53-54°). The purity of the compound was tested by TLC. I.R.(KBr): 1725, 1700, 970 cm^{-1} . Its 2,4 DNP derivative has m.p. 126-128° (lit.⁷, 127-128°) (Found: N, 15.34. Calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_6$: N, 15.40%).

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