Short Communication

Synthesis of ($\pm$)-2,3-*cis*-Stegobinone,
($\pm$)-*cis*-2,3-Dihydro-2,3,5-trimethyl-
6-(1-methyl-2-oxobutyl)-4*H*-pyran-
4-one, the Sex Pheromone of
Drugstore Beetle

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Stegobinone **4**, the sex pheromone of the drugstore beetle (*Stegobium paniceum* L.), has recently been isolated and its gross structure established as 2,3-dihydro-2,3,5-trimethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one by spectroscopic evidence^{1,2)} and biomimetic syntheses^{3,4)} of its stereoisomeric mixture. The absolute configurations at C2, C3 and C7 in the molecule have been assigned to be (2*S*,3*R*,7*R*) by several stereoselective syntheses^{5~7)} and, therefore, the relative configuration of the C2- and C3-methyls in the natural stegobinone is *cis*.

In this paper, we report a simple and efficient synthesis of ($\pm$)-2,3-*cis*-stegobinone **4**, which will surely bring us closer to developing a sensitive population monitor for this stored product pest.

4-Methylheptan-3,5-dione (1 mol) **1**, prepared from the acylation of diethylketone with propionic anhydride, was treated with acetaldehyde (2.5 mol) in the presence of boron trifluoride etherate (1 mol) with stirring for 2 hr at 5~10°C to give a 2,3-*cis/trans* mixture

(4:1) of 2,3-dihydro-2,3,5-trimethyl-6-ethyl-4*H*-pyran-4-one **3**⁷⁾ in a 75% yield.

Purification of the 2,3-*cis*-pyranone **3** was easily achieved by florisil column chromatography using a benzene-ethyl acetate mixture (9:1). The confirmation of the relative configuration of the C2- and C3-methyls in the pyranone was obtained by measuring the J_{H2-H3} values in a PMR spectrum ($J_{2,3-*cis*}=3.5$ Hz; $J_{2,3-*trans*}=12.0$ Hz).

Acylation at the methylene carbon in the ethyl substituent of the pyranone (1 mol) **3** with propionic anhydride (4.5 mol) in the presence of zinc chloride (2 mol) with stirring for 48 hr at 40°C, and followed by treatment with 60% sulfuric acid-methanol to decompose the corresponding enol ester, furnished 2,3-*cis*-2,3-dihydro-2,3,5-trimethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one (a mixture of diastereoisomers at C7) **4** with a retention of the 2,3-*cis* relative configuration in a 82% yield.

All spectral data for the synthetic ($\pm$)-2,3-*cis*-stegobinone **4** were identical with those of naturally-occurring stegobinone, except for some signals due to the co-existence of the C7-epimer.

The synthetic ($\pm$)-2,3-*cis*-stegobinone elicited a sex pheromone activity to the male drugstore beetle with a threshold concentration of approximately 10^{-3} mg/ml in a glass rod bioassay, by which naturally-occurring stegobinone showed a threshold of 10^{-4} mg/ml.

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