SYNTHESIS OF A COMPONENT OF THE AGGREGATION PHEROMONE OF Cryptolestes pusillus

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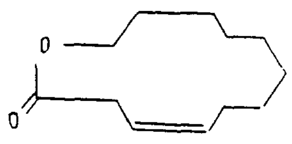
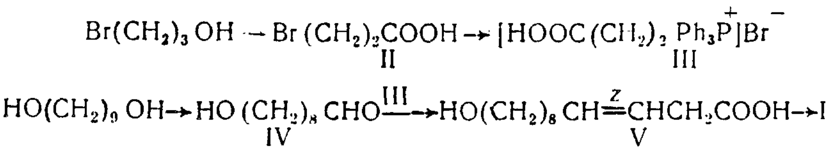
The flat grain beetle Cryptolestes pusillus is one of the widely distributed pests of grain and the products of its processing. Its aggregation pheromone includes three cyclic macrolides [1]. In the present communication we described the synthesis of one of them – dodec-3Z-enolide (I):



I

The synthesis of this component of the pheromone was carried out by the following scheme:



$$Br(CH_2)_3OH \rightarrow \underset{II}{Br(CH_2)_2COOH} \rightarrow \underset{III}{[HOOC(CH_2)_2\,Ph_3\overset{+}{P}]\overset{-}{Br}}$$

$$HO(CH_2)_9OH \rightarrow \underset{IV}{HO(CH_2)_8CHO} \xrightarrow{III} \underset{V}{HO(CH_2)_8CH\overset{Z}{=}CHCH_2COOH} \rightarrow I$$

Diethyl azelate was reduced with lithium tetrahydroaluminate. On interaction with a solution of tert-butyl chromate the nonane-1,9-diol so obtained gave 9-hydroxynonanal (IV). The extraction of the aldehyde (IV) formed was difficult, since the reaction produced a viscous resinous mass. The aldehyde was purified by column chromatography on silica gel (L 100/250, Chemapol) in the acetone–hexane (2:1) system.

3-Bromopropan-1-ol was oxidized by the Jones reagent at 0°C to the acid (II) with a yield of 75%. When the 3-bromopropionic acid (II) was boiled with triphenylphosphine in acetonitrile for 8 h, the phosphonium salt (III) was formed with 88% yield.

The key stage in the synthesis of the pheromone component was the Wittig reaction. As the base in the performance of this reaction we used potassium tert-butanolate, which was added to a solution of the phosphonium salt in dimethylformamide.

After two hours' stirring, the 9-hydroxynonanal was added in dimethylformamide at 0°C. The mixture was stirred for 3 h and was left overnight. Then it was extracted with benzene, and the extract was dried over Na_2SO_4 and filtered through Al_2O_3. After elimination of the solvent, the product was chromatographed on a column of Chemapol silica gel 100/250 in the ethyl acetate–hexane–acetic acid (50:100:1) system. Yield 60%. PMR (ppm): 1.15-1.65 (12H, m); 1.95-2.20 (2H, m); 2.9 (2H, d, J = 5.0 Hz); 3.64 (2H, t, J = 6.5 Hz); 5.52 (2H, m).

Cyclization of the acid (V) was achieved by the method of [2] using di-2-pyridyl disulfide. The reaction mixture – the acid (V), di-2-pyridyl disulfide, and triphenylphosphine in a molar ratio of 0.5:1:1 in xylene – was added dropwise in boiling xylene. Boiling was continued for 2 h, and then the xylene was distilled off and the residual oil was chromatographed on a column of Chemapol silica gel L 40/100 in the hexane–ethyl acetate (40:1) system. Yield 24%. The IR and PMR spectra of the product obtained were identical with those given in the literature [2]. Thus, a new route to the synthesis of dodec-3Z-enolide has been proposed.

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