DETECTION AND SYNTHESIS OF A SYNERGIST OF THE SEX PHEROMONE OF THE COTTON BOLLWORM

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The synergisic properties of docosa-5Z, 17Z-diene — one of the by-products of the synthesis of the synthetic cotton bollworm pheromone — have been revealed.

The isolation of compounds influencing the attractiveness of pheromones is no less important than the search for methods of synthesizing them, and this applies all the more to compounds having a high probability of formation in side reactions during the synthesis.

The synthesis of components of the pheromone of the cotton bollworm shifted long ago from the field of scientific developments to the field of practical application. In the synthesis by the acetylene route [1] of hexadec-11Z-enal (I) — the main component of this pheromone — the problem must be faced of purifying one of the initial synthons — a 10-halogenodecan-1-ol (II) — from a 1,10-dihalogenoalkane (III) impurity. The methods of column chromatography and also of countercurrent distribution [2], which serve admirably for the purification of small amounts, are practically unusable when it is a question of several kilograms. With ever-increasing production, this so greatly complicates the process of obtaining the cotton bollworm pheromone, which is expensive even without this, that its manufacture may simply become unprofitable. It is just this situation that impelled us to consider, in the first place, how the presence of the impurity (III) affects the attractiveness of the bollworm pheromone.

The condensation of compound (III) with hex-1-yne (scheme) forms docosa-5,17-diyne (IV). The possibility of this direction of the reaction is also confirmed by studies devoted to methods of synthesizing methylene-separated diacetylenic compounds [3]. The product of the reduction of (IV) – docosa-52,172-diene (V) – is an impurity in (I).

$$HO - (CH_2)_{10} - OH \xrightarrow{HCI} Cl - (CH_2)_{10} - Cl \xrightarrow{C_4H_9C = CH}$$
$$\longrightarrow C_4H_9C \equiv C(CH_2)_{10}C \equiv CC_4H_9 \xrightarrow{[H]} \rightarrow$$
$$\rightarrow C_4H_9CH \stackrel{z}{=} CH(CH_2)_{10}CH \stackrel{z}{=} CHC_4H_9$$

The diynic hydrocarbon (IV), not known in the literature, was isolated by preparative TLC as an impurity in the hexadec-1-yn-1-ol that is the key compound in the synthesis of the cotton bollworm pheromone. It was identified by mass, IR, and NMR spectroscopies and elementary analysis, and also by TLC and GLC in comparison with a model obtained by independent synthesis. The previously undescribed product of its reduction, (V), was identified in the same way. In order to investigate its influence on the attractiveness of (I), the amount of (V) required for field trials was accumulated by synthesis according to the scheme given above. Compound (III) was synthesized from decane-1,10-diol under conditions for the predominant formation of dihalogenoalkanes: boiling with conc. HCl in the presence of $ZnCl_2$ [4]. The subsequent alkylation and reduction were carried out by analogy with known procedures [1].

Studies of the influence of a number of compounds on the attractiveness of the cotton bollworm pheromone are known in the literature. Thus, an antipheromone activity of tetradec-9Z-en-1-ol acetate and formate, the inertness of hexadec-11Z-en-1-ol, and the synergistic effect exerted on the bollworm pheromone in the preence of a number of isomers of (I) have been reported [5]. The question of the influence of the dienic hydrocarbon (V) was not considered in this case.

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For trials under field conditions we took compound (I) containing different amounts of (V) and also artificially prepared mixtures of (I) and (V) in various ratios. The trials were carried out over three years, with different population densities of the cotton bollworm. The results of the field trials showed that compound (V) possessed no attractiveness, but certain additions of it to (I) led to a 1.3- to 2.3-fold increase in the activity of the latter. The synergistic effect did not depend on the method of use: it was possible to use in one pheromone trap compounds (I) and (V) either separately, in different dispensers, or mixed in a single dispenser. The only determining factor was their ratio, and at a certain ratio a further increase in the concentration of (V) led to the quenching of the synergistic effect.

EXPERIMENTAL

The compounds obtained were analyzed by GLC on a LKhM-80 instrument using as the stationary phase Apiezon L, 15%, on Chromaton N-AW, at a working temperature of 200-250°C with the carrier gas helium at a rate of 60 ml/min, the length of the column being 2 m. TLC was conducted with the use of Al_2O_3 and Silufol plates with the solvent system ethyl acetate-carbon tetrachloride (1:2); detection with iodine vapor.

Isolation of (IV). Compound (IV) was isolated from the main fraction of the product of the alkylation of hex-1-yne with 10-chlorodecan-1-ol. The product, containing 6% of the impurity, was first enriched with this impurity by the countercurrent distribution method [2]. By using the hexane – ethyl acetate (65% solution) system the level of impurity in a hexane solution of the product was raised to 57%. After the solvent had been distilled off, a compound with $R_f 0.84$ was isolated from the product by preparative TLC on Al_2O_3 . It was extracted from the Al_2O_3 with hexane. The solvent was distilled off, and the product was analyzed.

Mass spectrum (*m/z*): 302 (M⁺). IR spectrum (cm⁻¹): 2220 (C = C). NMR spectrum (δ , ppm) 2.03 (CH₂-C=, 8H, m), 1.1-1.4 (CH₂, 24H, m), 0.85 (CH₃, 6H, m); n_D²⁰ 1.4718.

$$k_2 = \frac{1}{[I]t} lg \frac{V_0}{V_t} M^{-1} \cdot \min^{-1},$$

Independent Synthesis. Preparation of (III). A mixture of 43.5 g of decanediol, 85 ml of conc. HCl, and 136 g of $ZnCl_2$ (1:4:4) was boiled for 2 h, hexane was added, and the organic layer was separated from the acid solution, washed with water, and dried over Na₂CO₃ The solvent was evaproated off, and the residue was distilled in vacuum. This gave 24.1 g (48%) of (III). mp 120-122°C (4 mm).

GLC of the product showed the presence of 94% of (III), 4% of (II), and 2% of unidentified compounds.

Preparation of (IV). A suspension in 100 ml of hexamethylphosphoramide of the lithium amide obtained from 4 g of lithium in 300 ml of liquid ammonia in the presence of 0.2 g of calcined iron nitrate was stirred for 0.5 h, and then 29 g of hex-1-yne was added dropwise, followed, after 1 hours' stirring, by 16 g of (III). The mixture was heated at 40-45°C for 15 h and was then cooled and was decomposed with ice water acidified with HCl. The product was extracted with ether, and the extract was washed with 10% HCl solution and with water to neutrality, and then it was dried over Na₂SO₄, the solvent was evaporated off, and the residue was distilled in vacuum. Yield 11.2 g (49%). The purity of the product according to GLC was 98%. bp 170-172°C (1 mm). The analysis of the product (mass, IR, and NMR spectra, GLC and TLC) gave results similar to those for compound (IV) isolated from the reaction mixture by preparative TLC.

Preparation of (V). Compound (IV) was reduced over a nickel boride catalyst under conditions leading to the predominant formation of cis- isomers [1].

In a hydrogenation apparatus, a solution of 0. 5 g of NaBH₄ in 25 ml of ethanol, 1.5 ml of 70% aqueous ethylenediamine in 10 ml of ethanol, and 21 g of (IV) in 50 ml of ethanol were addd to 4 g of $(CH_3COO)_2Ni \cdot 4H_2O$ in 200 ml of ethanol. After the absorption of hydrogen had ceased, the suspension was passed through a layer of silica gel, and this was washed with ether. The solution was treated with 10% HCl and with water, and was dried with Na₂SO₄ and distilled in vacuum. This gave 14.9 g (70%) of (V), bp 163-165°C (1.0 mm), n_D^{20} 1.4591, R_f 0.98.

Mass spectrum (m/z): 306 (M⁺). NMR spectrum (δ , ppm): 5.25 (CH=CH), 4H, m); 2.01 (CH₂-CH=, 8H, m); 1.25 (CH₂, 24H, m); 0.86 (CH₃, 6H, m).

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