STUDY OF THE STABILIZATION OF cis-HEXADEC-11-ENAL — THE MAIN COMPONENT OF THE SEX PHEROMONE OF THE COTTON BOLL WORM — BY TOCOPHEROL

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The stabilization of cis-hexadec-11-enal — the main component of the sex pheromone of the boll worm — by additions of tocopherol has been studied by UV spectroscopy. It has been shown that the addition of 2-2.5% of tocopherol considerably increases the stability of the attractant.

Under the action of a number of environmental factors (sunlight, atmospheric oxygen, temperature, etc.), many sex pheromones of insects are rapidly decomposed with the loss of their biological activity [1]. Such antioxidates as Ionol, tocopherol, arylamine derivatives, and a number of other substances are used as stabilizers for sex pheromones [2-4]. Field trials of preparative forms with the sex pheremone of the cotton boll worm have shown that they rapidly lose their activity with respect to males of the pest and require repeated replacement in the course of the field season. The greatest attractiveness for males of the cotton boll worm is possessed by a two-component synthetic sex pheromone consisting of a mixture of cis-hexadec-11-enal and cis-hexadec-9-enal (9:1) [5].

The present work forms the beginning of systematic investigations by UV spectroscopy of the possibility of statilizing synthetic sex pheromones of cotton pests by additions of various antioxidants. Here we give the results of investigations on increasing the stability of the synthetic sex pheromone of the cotton boll worm by the addition of the antioxidant tocopherol. Tocopherol is widely used as a stabilizer of various natural substances, but its stabilizing action on pheromones has been little studied. Furthermore, it does not possess repellent properties in relation to the males of the cotton boll worm.

In UV spectra of samples of the main component of the pheromone, cis-hexadec-11-enal, a characteristic absorption peak was observed in the 230-340 nm region with its maximum at a wavelength of 280 nm. In the process of exposure of the samples at a temperature of 45°C under UV irradiation, as the result of the decomposition of the cis-hexadec-11-enal the intensity of absorption at this wavelength decreased (Fig. 1). The addition of tocopherol did not change the nature of the UV spectra, in view of which the decomposition of the cis-hexadec-11-enal was evaluated from the decrease in the value of the optical density at λ 280 nm.

The decomposition of the substance was calculated as a percentage from the formula

$$\text{Decomp.} = \left(1 - \frac{D^1_{\lambda\,280}}{D^0_{\lambda\,280}}\right) \cdot 100,$$

where $D^0_{\lambda 280}$ and $D^1_{\lambda 280}$ are the optical densities of a solution of the sample being analyzed before and after irradiation, respectively.

The amount of tocopherol added ranged from 0 to 2.5% on the attractant. The results of the experiments are presented in Table 1.

It can be seen from Table 1 that the decomposition of cis-hexadec-11-enal without the addition of the stabilizer under UV irradiation took place very rapidly, and 58.5% of the substance had decomposed after 5 h. The addition of 0.25 wt.% of tocopherol created an insignificant stabilizing effect in the first 3 h of irradiation. An increase in the amount of tocopherol to 0.5 wt.% lowered the decomposition of the cis-hexadec-11-enal after irradiation for 5 h to 50%. The addition of 2.0-2.5% of the antioxidant considerably increased the stability of the attractant. It underwent practically no decomposition during irradiation by UV light for 1.5 h, and after irradiation for 5 h it was 37% decomposed.

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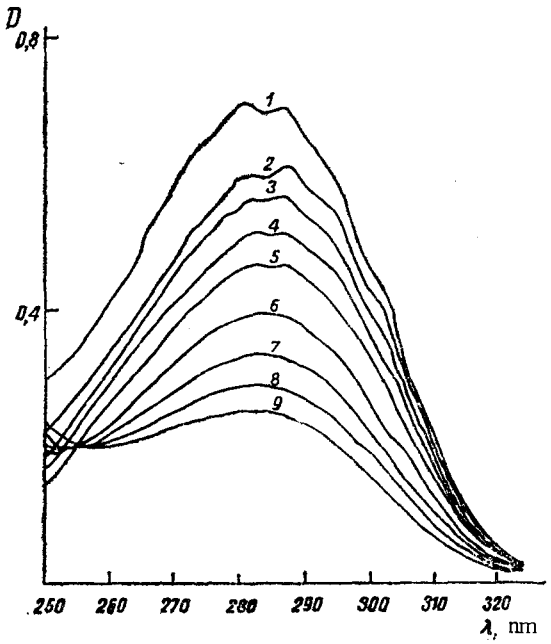

Fig. 1. Change in the optical density of cis-hexadec-11-enal as a function of the time of UV irradiation (h): 1) 0; 2) 0.5; 3) 1, 4) 1.5; 5) 2; 6) 3; 7) 4; 8) 5, 9) 6.

TABLE 1. Dependence of the Degree of Decomposition of cis-Hexadec-11-enal on the Amount of Stabilizer Added and the Time of UV Radiation at 45°C

Tocopherol, % on the attractant	Decomposition (%) at the following times of irradiation, h						
	0,5	1	1,5	2	3	4	5
0	14,6	20,8	26,7	34,7	44,6	52,5	58,5
0,25	10,9	14,6	20	27,3	41,9	50,9	58,2
0,5	6,0	10	14	21	36	43	50
1,0	0,9	6,8	10	15,3	28,8	35,6	47,5
2,0	0	0	0	3,3	19,7	26,7	36,9
2,5	0	0	2,4	8,0	20	34,4	37,5

We also studied the efficacy of the stabilizing effect of the addition of 2% of tocopherol to cis-hexadec-11-enal under the conditions of artificial aging without UV irradiation at 37°C. It was found that the complete decomposition of the attractant required 100 h, while a stabilized sample underwent only 9% decomposition during this time.

As Shaver [6], who studied the decomposition of cis-hexadec-11-enal on storage at room temperature and under fluorescent radiation, has shown, decomposition took place with the formation of 12 different products. The main decomposition products proved to be cis-hexadec-11-enoic acid, cis-11,12-epoxyhexadecanoic acid, and cis-11,12-epoxyhexadecanal, i.e., the decomposition of the cis-hexadec-11-enal takes place by the following main mechanism: oxidation of aldehyde group to a carboxyl group, and epoxidation of the double bond. It is probable that the decomposition of the substance under more severe conditions (UV irradiation at a temperature of 45°C) takes place in the same way and the addition of tocopherol, which inhibits free-radical reactions through the presence of the mobile hydrogen of a hydroxy group in an aromatic ring, raises the stability of the cis-hexadec-11-enal.

Since one of the degradation products — cis-11-12-epoxyhexadecenal, which retained no biological activity — can probably absorb at the same wavelength as the active cis-hexadec-11-enal, in order to establish a correlation between the biological activity and the optical density we have planned to perform trials of the stabilized attractant under field conditions.

EXPERIMENTAL

UV spectra were recorded on a Specord M-40 instrument. An OKM-9 lamp was used as the source of UV light.

To obtain a series of solutions containing from 0.25 and 2.5 wt.% of tocopherol on the attractant, test-tubes were charged, respectively, with 1.4, 2.2, 4.4, 8.8, and 10.75 μl of a 5% solution of tocopherol in hexane, to each was added 21.8 mg of cis-hexadec-11-enal, and the volume was made up with hexane to 1.3 ml. The solutions were transferred into quartz cells with ground-in lids. Solutions of tocopherol in hexane in the same concentrations

as in the samples under test were placed in comparison cells. The absorption spectra of the solutions were recorded and then they were subjected to UV irradiation at 45°C. The distance from the cells to the source of irradiation was 25 cm. After predetermined intervals of time, the optical densities of the solutions were measured at the wavelength maximum of 280 nm and the decomposition of the cis-hexadec-11-enal was calculated from the formula given above. All the experiments were performed in duplicate. The artificial aging (without UV irradiation) of test samples was carried out in sample bottles with ground-in stoppers in a thermostat at 37°C.

CONCLUSIONS

The decomposition of cis-dexadec-11-enal under the conditions of UV irradiation and of artificial aging without and with the addition of tocopherol has been studied by UV spectroscopy. It has been shown that the addition of 2-2.5% of tocopherol to samples of cis-hexadec-11-enal considerably increases its stability.

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