ANALYSIS OF THE PRODUCTS OF SYNTHESIS OF THE PHEROMONE OF THE BOLLWORM BY GAS-LIQUID CHROMATOGRAPHY

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The possibility has been shown of the effective separation and identification of the main component of the pheromone of the bollworm, hexadec-cis-11-enal, and accompanying impurities by gas-liquid chromatography on the nonpolar stationary liquid phase E-301 deposited on Chromaton N-AW-HMDS.

Synthetic pheromones are widely used in the fight against pests of the cotton plant and other agricultural crops. Hexadec-cis-11-enal is one of the main components of the sex pheromone of the bollworm [1, 2]. The aim of our work was to determine by gas-liquid chromatography the composition of the products of the synthesis of the bollworm pheromone and to develop a chromatographic method of analysis for monitoring the synthesis.

We synthesized hexadec-cis-11-enal by the acetylene route: lithium hexynylide was alkylated with 10-bromodecan-1-ol, and the hexadec-11-ynol formed was reduced stereoselectively to hexadec-cis-11-en-1-ol, which was converted by the action of pyridine chlorochromate into the hexadec-cis-11-enal.

The main component of the pheromone and the accompanying impurities formed during the synthesis were isolated in the individual form by column chromatography. As a result, 10-bromodecan-1-ol, 1,10-dibromodecane, hexadec-11-yn-1-ol, hexadec-cis-11-en-1-ol, and hexadec-cis-11-enal were obtained. Qualitative determination was performed with the aid of TLC, and the IR spectra of the products were recorded to determine their nature.

Various stationary liquid phases are used to separate pheromones by gas-liquid chromatography [3, 4]. We used liquid phases with different polarities of the type of Apiezon L, Apiezon N, OV-225, silicone XE-60, the methylsilicone elastomer E-301, dinonyl phthalate, and UZhF (Institute of Chemistry of the Uzbek SSR Academy of Sciences, Tashkent). The nonpolar liquid phase E-301 proved to be the most selective of them. The efficiency of separation of other liquid phases was considerably lower, and no clear and complete separation of the components was achieved.

To find the optimum region of separation, chromatograms were taken of the isolated individual substances and of experimental samples from the synthesis of the pheromone at column thermostat temperatures of 160, 170, 180, and 200°C on the polyphase sorbent 10% E-301—Chromaton N-AW-HMDS. Below, we give the retention times in minutes of the individual substances and of an experimental sample on the liquid phase E-301 at various column temperatures:

Substance	160°	170°	180°	200°	Experimental sample, 180°
10-Bromodecan-1-ol	20,6	15,3	7,0	1,6	7,3
1,10-Dibromodecane	24,6	18,0	10,3	2,0	10,3
Hexadec-cis-11-enal	34,0	24,6	13,6	4,0	13,9
Hexadec-cis-11-en-1-ol	39,3	28,0	17,5	4,1	17,8
Hexadec-11-yn-1-ol	45,3	32,0	20,0	6,3	20,9

As can be seen from these results the retention times of the components decreased sharply at a column temperature of 200°C and the issuing components overlapped. The most complete separation was observed at 160°C, but in this case, because of the very long retention times, the chromatogram was stretched out. The optimum temperature of separation was 180°C, where the retention times were shortened almost threefold and the chromatogram had clearly

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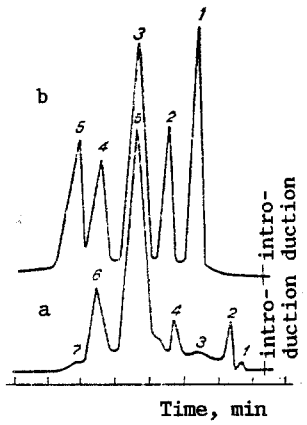

Fig. 1. Chromatograms of the bollworm pheromone (a) and of an artificial mixture of individual substances (b) in the liquid phase E-301: (b): 1) 10-bromodecan-1-ol; 2) 1,10-dibromodecane; 3) hexadec-cis-11-enal; 4) hexadec-cis-11-en-1-ol; 5) hexadec-11-yn-1-ol.

separated peaks. The selectivity of the liquid phase E-301 with respect to the substances being separated was established by comparing the relative retention volume V_{rel} of the individual substances (ISs) and the experimental sample (ES) at a column temperature of 180°C relative to hexadec-cis-11-en-1-ol:

	V_{rel} of the IS	V_{rel} of the ES
Hexadec-cis-11-enal	0,77	0,77
Hexadec-cis-11-en-1-ol	1,00	1,02
Hexadec-11-yn-1-ol	1,14	1,19

Identification was carried out by introducing the individual substances into experimental samples and comparing their retention times. The substances introduced artificially gave increases in the corresponding peaks in the chromatogram. Figure 1 shows chromatograms of an artificial mixture of individual substances and of an experimental sample of the bollworm pheromone. The first two peaks have not been identified.

The amounts of the main component of the pheromone and of the impurities in the experimental samples were calculated from the results of chromatographic separation on the given column. The main component of the pheromone, hexadec-cis-11-enal, amounted to 88-95% and the level of 1,10-dibromodecane ranged from 0.75 to 1.47%; in some samples 0.35-0.67% of 10-bromodecan-1-ol and 0.84-3.43% of hexadec-cis-11-en-1-ol were detected. Also in some samples a trace amount of hexadec-11-yn-1-ol was found.

The percentage contents were calculated from the ratio of the area of the peak of the component being determined to the total area of all the peaks [5, 6]:

$$A = \frac{\text{area of peak of A}}{\text{total area of the peaks}} \cdot 100.$$

Quantitative analysis was carried out by the method of "internal normalization." Substances obtained in the synthesis of the pheromone were used as standards: 10-bromodecan-1-ol, 1,10-dibromodecane, hexadec-cis-11-en-1-ol, hexadec-cis-11-enal, and hexadec-11-yn-1-ol, and chemically pure hex-1-yne and decane-1,10-diol. The purity of the standards determined beforehand by the GLC method was 95-98%.

EXPERIMENTAL

The main component of the bollworm pheromone and the impurities accompanying the synthesis of the pheromone were isolated by column chromatography. Glass column (V = 50 ml) filled with silica gel KSK (0.100-0.200 mm). The solvents used were hexane and hexane–benzene (19:1) with a subsequent increase in the proportion of benzene. Fractions with a volume of 15 ml were collected. Fractions 1-4 (eluted by hexane) yielded 1,10-dibromodecane. On further elution, hexadec-cis-11-en-1-ol, hexadec-cis-11-enal, hexadec-11-yn-1-ol, and 10-bromodecan-1-ol were obtained. Sulufol UV-254 plates were used for TLC. The following solvent systems were used for running the chromatograms: hexane–ethyl acetate (1:1), (4:1), and (11:1), and also hexane–benzene (19:1), (9:1), (17:3), and (4:1), and pure hexane. The plates were visualized in an iodine chamber followed by spraying with water, and also without an iodine chamber and spraying with concentrated H_2SO_4.

The isolated individual components of the experimental samples were separated on a Chrom 5 gas-liquid chromatograph (Czechoslovakia) with a flame-ionization detector.

The methylsilicone elastomer E-301 was used as the stationary liquid phase. The amount of liquid phase was 10% of the weight of the solid support, Chromaton N-AW-HMDS (0.50-0.25 mm fraction). The liquid phase was deposited on the solid support from solution in benzene by the rotating-flask method. Glass columns with dimensions of 3 mm × 3.5 m were used. Separation was carried out at temperatures of 160-200°C, at a rate of flow of the carrier gas, helium, of 30 ml/min, a sensitivity of the detector of 100:10,000/128, a chart speed of 0.3 cm/min, and a volume of the sample introduced of 0.02 μl. The samples were injected with the aid of an MSh-10M microsyringe.

SUMMARY

The possibility of the effective separation and identification of the main component of the bollworm pheromone hexadec-cis-11-enal and the accompanying impurities by gas-liquid chromatography on the nonpolar liquid phase E-301 deposited on Chromaton N-AW-HMDS has been shown.

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