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The influence of UV irradiation on the synthetic pheromone of the grape moth *Lobesia botrana* (Lepidoptera: Tortricidae)

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Rezumat

Influenţa razelor UV asupra feromonului sintetic al moliei strugurilor *Lobesia botrana* (Lepidoptera: Tortricidae)

Feromonul sintetic al moliei strugurelui *Lobesia botrana* a fost expus la raze UV (302nm). Acesta a fost examinat înainte si după expunere cu ajutorul unui GC-MSD. S-a discutat structura câtorva produşi de degradare. Materialului modificat i sa testat puterea de captare in câmp. Capcanele feromonale şi-au pierdut atractivitatea faţă de specia *Lobesia botrana*, însă au atras insecte aparţinând altor specii (*Cydia pomonella, Lymantria dispar*).

Abstract

The synthetic pheromone of the European grape moth *Lobesia botrana* was exposed to UV light (302nm). It was examined before and after exposure by means of a GC-MSD. The structure of several degradation products was discussed. The attractiveness of the irradiated samples to moth was tested by field trapping. The degradation products did not attract *Lobesia botrana*, but did attract insects belonging to other species (*Cydia pomonella*, *Lymantria dispar*).

Keywords: *Lobesia botrana*, European grape moth, Lepidoptera, Tortricidae, (E,Z)-7,9-12 OAc, sex pheromone, UV radiation, field traps tests, vineyard

Introduction

The degrading effects of UV light on pheromones with conjugated double bonds have been studied both in field (in sunlight) and in laboratory conditions (SHANI & KLUG 1980a, b, SHANI et al. 1982, IDESES et al. 1982a, MILLAR 1995, PANADES 1998).

As the pheromone samples were exposed to UV in the presence of the atmospheric air, besides isomerisation also oxidation was observed, both reactions involving a radicalic mechanism (SHANI & KLUG 1980a, b, SHANI et al. 1982, IDESES et al 1982B, IDESSES & SHANI 1989).

In order to protect the pheromones from isomerisation and oxydation, UV stabilizers and antioxidants were used (IDESES et al 1982b, IDESSES & SHANI 1986, 1987, 1988, MILLAR 1995).

In the present work, the degradation velocity of the conjugated diene pheromone of *Lobesia botrana* and the chemical structure of several degradation products were studied. In addition, the attractivity of the products to moths was studied in the field.

Methods and Materials

Pheromones

The main component of the sex pheromone of *Lobesia botrana* BUSER et al. (1974) has been identified as (E,Z)-7,9-dodecadien-1-yl acetate, (E,Z)-7,9-12 OAc.

The pheromone and the pheromone baits used in this work were provided by the Institute of Chemistry „Raluca Ripan" Cluj-Napoca.

UV Irradiation

The exposure of the *Lobesia botrana* pheromone to UV occurred in synthetic quartz (pure $SiCl_4$) vials (5ml), hermetically closed with SCHOTT GL14 lids, made of PBT°, with teflon filling. These

allow the penetration of UV light of wave lengths between 170nm to 2000nm. The UV light (302nm) was obtained from a „Mini-Transilluminator", number 462BR1029, from BIO-RAD. This device has an emitting area of 21cm x 26cm, 6UV lamps, input voltage / frequency: 220-240 VAC/50-60 Hz and 150 W.

For exposure two groups of 5 quartz vials were used, each of them loaded with 2µl of pheromone. Every 15 min of exposure, the concentration of the (E,Z)-7,9-12 OAc have been determined by means of the GC-MS. The vials exposed to UV for the field experiments contained 8µl pheromone and were exposed for 21 hours under the same conditions.

GC-MS

The degradation products were determined by means of a gas chromatograph-mass spectrometer, model HP-5890II/5972. The gas chromatograph had a HP-5MS column, 30m long, with a diameter of 0.25 mm, and thickness of the filling film of 0.25 µm. This method allowed to record masss up to 350 units; the temperature program is shown in Tab.1.

The initial temperature was 100° C, with an initial time of 2 min. The injection of the samples was automatic, the solvent used was n-hexane.

Traps

The adhesive traps that have been used were a Delta type delivered by W. Neudorff GmbH KG, 31860 Emmerthal.

The field test took place between July, 25 and August, 23, 1998. The traps were placed in a vineyard, each of them baited with 1µl of the *Lobesia botrana* pheromone as follows:

- 8 traps containing the fresh pheromone,
- 8 traps containing the pheromone exposed to UV.

The vineyard had an area of 2000m², and was cultivated according to biological methods, where no insecticides or herbicides were used.

The traps were hung at distances of 10-15 m between each other. This vineyard was adjacent especially on its sides to other vineyards.

Also at every three days the position of the traps was changed as shown in Fig. 1.

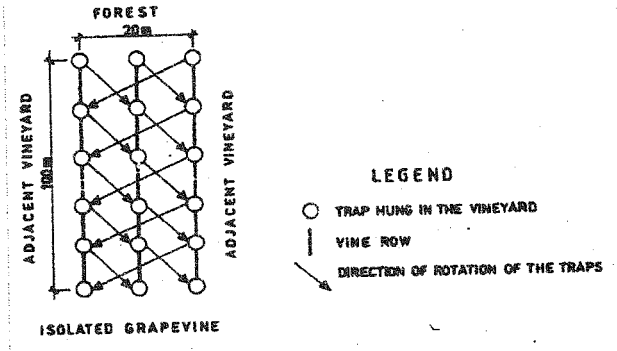


Fig. 1. The vineyard and the rotation of the traps

Results and discussion

Labor trials

The concentration of the (E,Z)-7,9-12 OAc (retention time 10.05 ± 0.03 minute) decreased to zero after 60 min of exposure to UV (Fig. 2).

In Fig. 3, the (E,Z)-7,9-12 OAc appears at 10.07 min; at 10.23 min appears its (E,E) isomer (BUSER AT AL. 1974).

During the exposure a degradation product appears, which has almost the same retention time as the (E,Z)-7,9-12 OAc (10.02 min in Fig. 4). The lower the concentration of the pheromone, the higher was that of the degradation product. Th is phenomenon is similar to that described by OLDENBURG ET AL. (1999) for degradation of the *Lobesia botrana* pheromone due to heating.

As seen in the Fig. 4, there are numerous degradation products.

The degradation products with a retention time of 10.02 and 11.54 min have similar mass-spectra,

Table 1.

The temperature program used in the GC-MS analysis

Level	Rate (°C/min)	Final temp (°C/min)	Final time (min)
1.	40.00	140	0.00
2.	5.00	220	0.00
3.	60.00	280	2.00

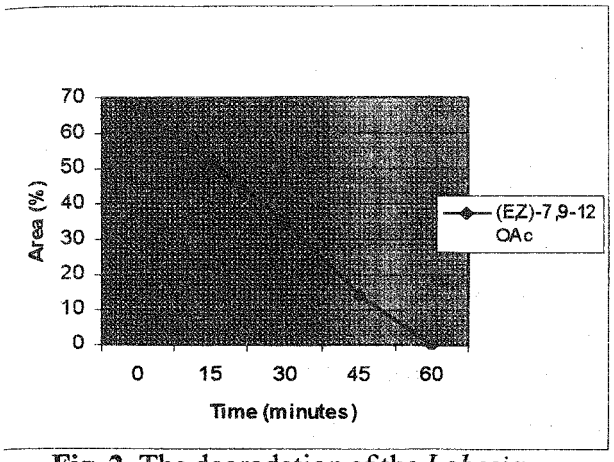


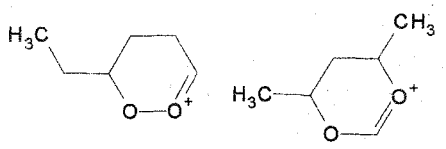
Fig. 2. The degradation of the *Lobesia botrana* pheromone under the influence of the UV irradiation

and the main peak m/z 115 are followed by the ions m/z 69 and m/z 43. The ion m/z 115 could have the structure of a peroxide (*a)* or 1,3-dioxane (*b)* as shown below, olso observed after exposure of the *Lobesia botrana* pheromone to heat in the presence of air (OLDENBURG ET AL. 1999):

The peak at 10.35 min (Fig. 4) is, most likely, an 2-ethyl-5-hexylacetate-furan (structure shown below) which is easily recognizable from the mass-spectrum of the ion m/z 109 (SHANI & KLUG 1980A, IDESES ET AL. 1982B).

Other peaks of smaller intensity will be analysed in the following.

The component with the retention time 7.35 min (Fig. 4) has most likely the structure of an acetic



a, m/z 11 b, m/z 11

ester with 10 carbons ($C_{10}H_{18}O_2$), with M=170, which

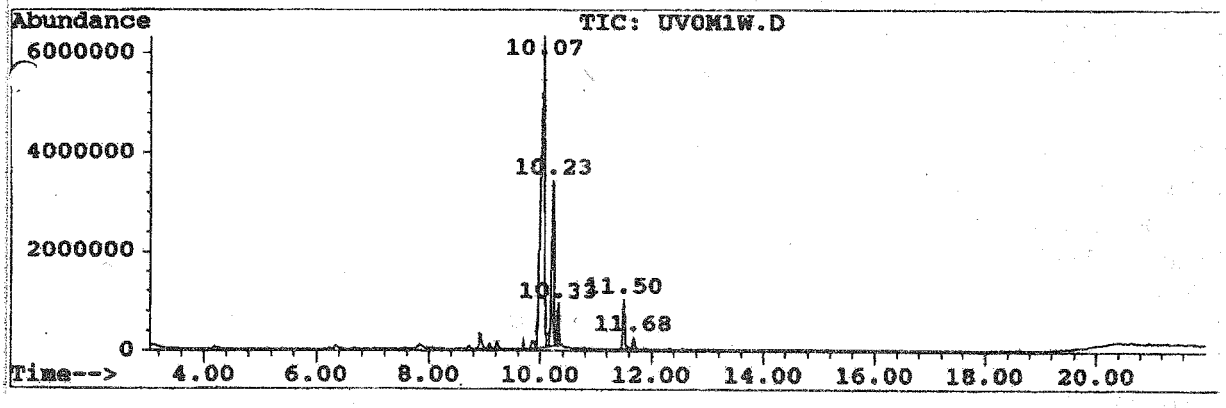


Fig. 3. Chromatogram of the *Lobesia botrana* pheromone, control sample of fresh pheromone

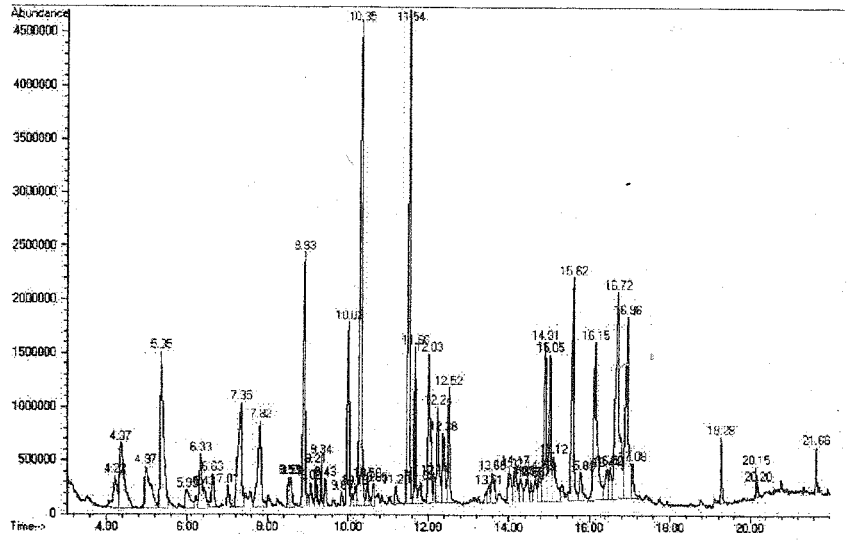
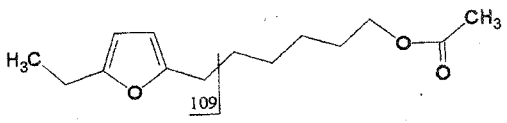


Fig. 4. Chromatogram of the *Lobesia botrana* Pheromone, sample exposed 60 min to UV

would correspond to the octadienylacetate.

As can be seen in Fig. 5, the mass-spectrum contains the ion m/z 110 formed after the elimination of a molecule of acetic acid, with mass 60, through a McLafferty transposition (BUDZIKIEWICZ 1992). The



M=238

ion m/z 127 results from the molecular ion loosing a propyl radical with mass 43. The ion m/z 60 corresponds to the acetic acid resulting from a McLafferty transposition typical to methyl esters. The ion m/z 61 results from a double transposition of hydrogen, indicating the presence of the hydrogen in the position ß and γ from the alcoholic chain. The fragment 43 is particular to the acetates and has the structure $CH_3—C\equiv\overset{\oplus}{O}$ (OPREAN 1974).

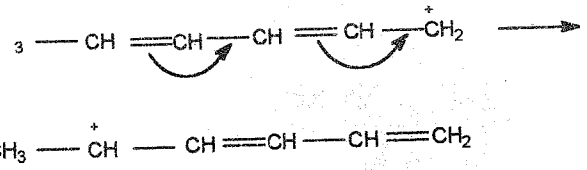
The intensity of the hydrocarbonate ions type C_nH_{2n+1} 29, 43, 57, 71, 85, 99, 113 and 127, type C_nH_{2n-1} 41, 55, 69, 83, 97, 111, 125 and type C_nH_{2n-3} 39, 53, 67, 81, 95, 109, 123, 137 and 151 support the presumption of a chain with a single double bond.

The component with the retention time 7.82 min, M=170, could have an octenyl acetate structure. The mass-spectrum of this peak presents the ion m/z 110, resulting as above, from the loss of the acetic acid molecule. The ions m/z 61 and m/z 43 correspond to the protonated acetic acid respectively $CH_3—C\equiv\overset{\oplus}{O}$. These ions are particular to the acetic esters.

The ions m/z 141 and m/z 127 result from the molecular ion, after elimination of the ethyl and propyl radicals. In conclusion, the two components with the retention time 7.35 and 7.82 min (Fig. 4) could be isomers.

Fig. 6 presents the mass-spectra of the compound with the retention time 8.93 min (Fig. 4) compared to that of the (Z)-6-decenyl acetate, mentioned by Wiley 275 (Spectrum Library) as the most probable structure. Both have the molecularmass 198 and the ion m/z 138 is M-acetic acid (60). The type of ions in the two spectra are identical, but of different intensity. The ion m/z 81 whose structure is presented below, shows an increased stability due to resonance, resulting in its rather high intensity.

Since we cannot accurately determine the position of the double bond from the mass-spectrum for the peak in question, we remain at the structure of a decenyl acetate.



The mass-spectrum of the peak at 12,03 min (Fig. 4) is presented in Fig. 7. The molecular ion m/z 240 and the ions m/z 197 (M-propyl), m/z 180 (M-acetic acid), m/z 61 (the ion of the protonated acetic acid) and m/z 43 $CH_3—C\equiv\overset{\oplus}{O}$ are typical for an alkyl acetate. This substance has a mass with 16 units more than that of the initial dodecadienyl acetate, which could correspond to an additional atom of oxygen.

For this compound we propose the structure of a epoxydic derivate of the starting (E,Z)-7,9-12 OAc, probably with the epoxy function in the position

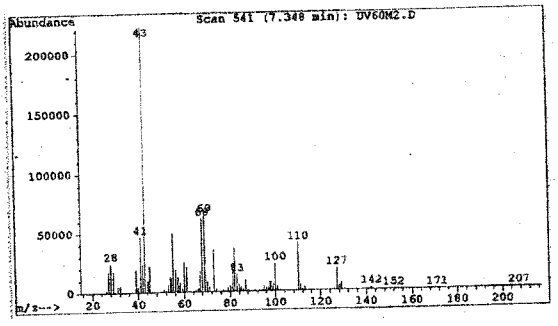


Fig. 5. The mass-spectrum of the compound with the retention time of 7,35 min in Fig. 4

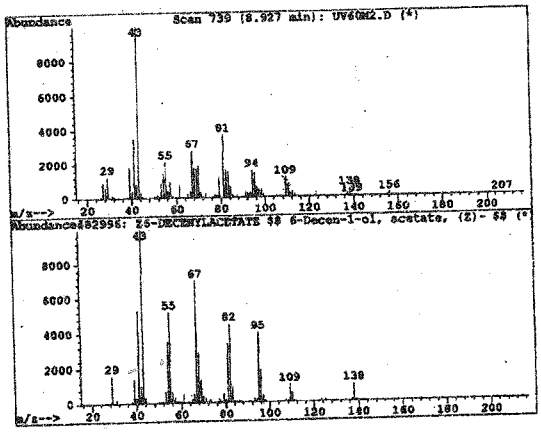
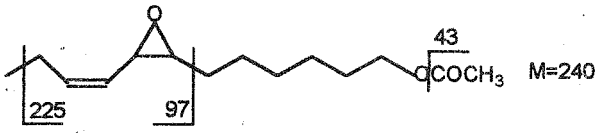


Fig. 6. The comparison of mass-spectra of the searched compound with retention time 8,93 min in Fig. 4 and that of the (Z)-6-decenyl acetate

7-8. The ion m/z 225 (M-15) could support this presumption, resulting from a scission of a methyl radical in the allylic position.



The ions m/z 211 (M-formyl radical) and m/z 151 (M-acetic acid and formyl radical) support the presumption of an epoxy derivate. The ion m/z 151 could eliminate three neutral molecules of ethene, resulting in the ion m/z 123, m/z 95 and m/z 67.

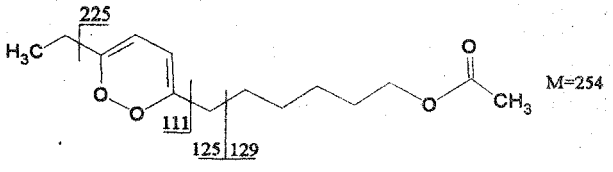
The ion m/z 81 has six carbon atoms and is stabilizated by resonance, which explains its high intensity in the mass-spectrum.

The peak of 15.05 min from Fig. 4 (mass-spectrum in Fig. 8) with the molecular ion m/z 254, is with 16 mass units larger than that of the alkyl furan, with the retention time of 10.35 min in Fig. 4 and M=238. Both spectra contain an intense ion m/z 109.

In the mass-spectrum one finds the ions m/z 225 (M-ethyl), m/z 212 (M-propyl), m/z 165 (M-acetic acid and ethyl radical), the ions m/z 61 and m/z 43, which prove the structure of the alkyl acetate.

Thus it can be supposed, that the product has the structure of an alkyl acetate grafted on a peroxydic cycle.

The ion m/z 125 forms up through a scission in an allylic position and the ion m/z 111 through an onium-reaction (HESSE & AL.1984). The ion m/z 125 could eliminate an atom of oxygen resulting in the fragment m/z 109, both 109 and 111, with a rather high intensity in this mass-spectrum.



The compound of 15.62 min (Fig. 4) with the mass 254, could be an isomer of the previous degradation product with a retention time of 15.05 min, having the same type of ions, but differing only in their intensity.

In Fig. 4 at 19.28 min appears the peak of an dienyl acetate with the mass m/z 308, this is 84 mass units bigger than the mass of the (E,Z)-7,9-12 OAc. This difference could be due to six additional carbon atoms ($6xCH_2$). The ion m/z 248 from the mass-spectrum (Fig. 9) is the result of the elimination of a neutral molecule of acetic acid resulting from the McLafferty transposition. The ions m/z 61 and m/z 43 are also typical for the scission of the acetate.

The intensity of the hydrocarbonate ions (Fig. 9) type C_nH_{2n+1}, type C_nH_{2n-1} and type C_nH_{2n-3} support the presumption of a chain with two double

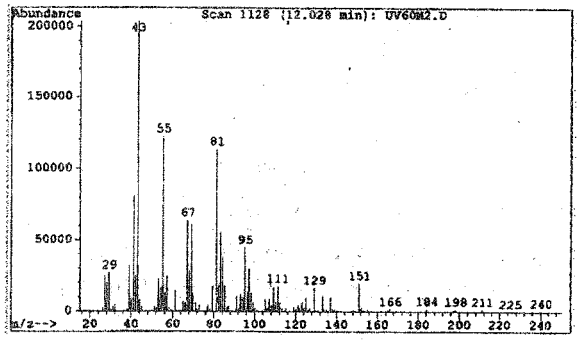


Fig. 7. The mass-spectrum of the compound with the retention time of 12.03 min (Fig. 4)

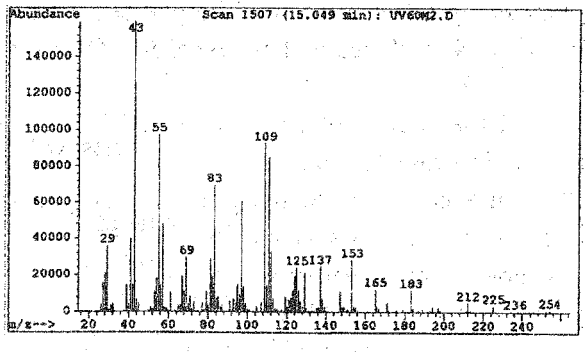


Fig. 8. The mass-spectrum of the compound with the retention time of 15.05 min (Fig. 4)

bonds.

This structure is most probably the octadecadienyl acetate.

Vineyard experiments

After the UV irradiation of the quarz containers with pheromone (8µl), we observed the formation of a yellowish colouring on the walls of the vials. This reminds of the unidentified resinuous material obtained by SHANI & KLUG (1980b) in the case of the prodlure, (Z,E)-9,11-tetradecadienyl acetate, the main component of the female sex pheromone of *Spodoptera littoralis*, after heating or exposure to sunlight without solvent for 2-4 days.

The modified pheromone was dissolved in two fractions: the first in hexan and the second in acetone.

The yellowish colouring dissolved only in acetone.

The compositions of compounds dissolved in the two solvents differed, as can be seen in Fig.s 10 and 11:

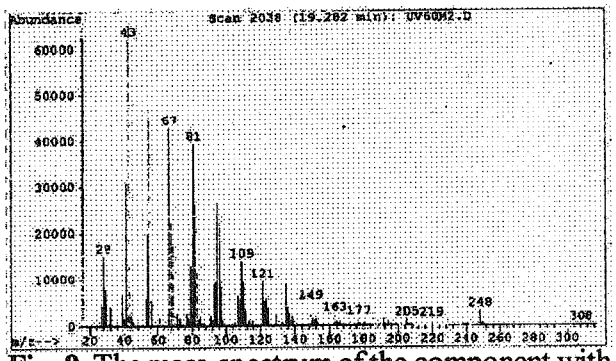


Fig. 9. The mass-spectrum of the component with the retention time 19.28 min (Fig. 4)

Fig. 10 presents three degradation products in higher concentrations with the retentions times: 9.55 min, 9.92 and 11.06 min. They are identical to those obtained by the irradiation of the pheromone for 60 min (Fig. 4) and also by heat exposure (OLDENBURG et al. 1999).

Other peaks of smaller intensities will be analysed in the following.

The component with the retention time of 7.35 min (Fig. 10) has the mass-spectrum shown in Fig. 12. The molecular ion appears at m/z 210, which together with the ion m/z 150 (M-acetic acid) resulting from a McLafferty transposition, and the ions m/z 61 and m/z 43 point to the acetate structure.

This component, having M=210 is 14 mass units smaller than that of the intact *L. botrana* pheromone. We could conclude, that this compound, the

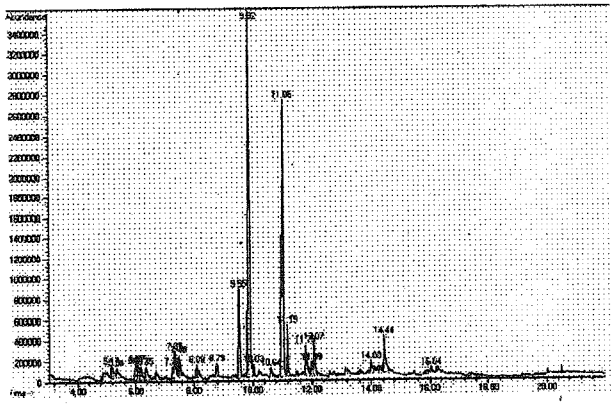


Fig. 10. Chromatogram of the *Lobesia botrana* pheromone, sample exposed 21 hours to UV, hexane extract

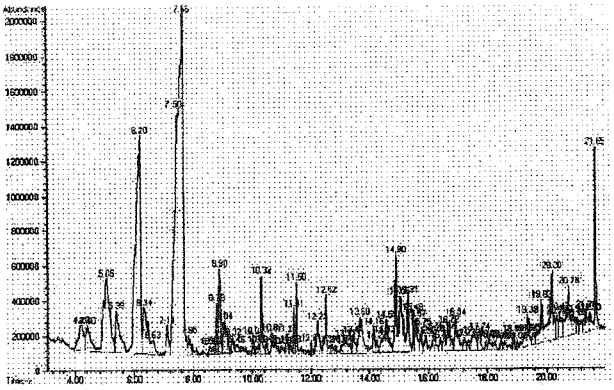
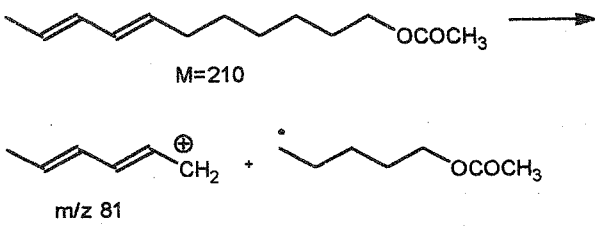


Fig. 11. Chromatogram of the *Lobesia botrana* pheromone, sample exposed 21 hours to UV, acetone extract

undecadienyl acetate, has the structure of the *L. botrana* pheromone, except that one carbon atom is missing. The conclusion is supported by the presence of the ions m/z 167 (M-propyl radical), m/z 135 (M-acetic acid and methyl radical), m/z 121 (M-acetic acid and ethyl radical) and ion m/z 107 (M-acetic acid and propyl radical).

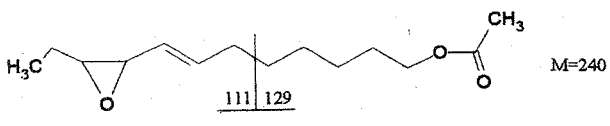
The ion m/z 81 is the main peak in this mass-spectrum; its stability is increased by resonance, as mentioned above. It results from an allylic scission as follows:



The component with the retention time of 11.79 min (Fig. 10) with the mass-spectrum in the Fig. 13 is similar to that of the peak 12.03 min (Fig. 7). This suggests an acetate with mass 240, probably having the epoxy group in position 9-10, which splits in allylic position as shown below, resulting in the peaks m/z 129 and m/z 111.

The ions m/z 180 (M-acetic acid), m/z 61 and m/z 43 point to the acetate structure.

The ion m/z 151 (M-acetic acid and ethyl radical or formyl radical) supports the peroxydic structure. The ethyl radical could results from position 1-2 or 11-12.



The mass-spectrum of the component with the

retention time of 14.44 min (Fig. 10) presented in Fig. 14, indicates also an acetate (M=256), two mass units larger than the compound with the retention time 15.05 min (Fig. 4) with the mass-spectrum in Fig. 8. The component at 14.44 min is also 32 mass units larger than the (E,Z)-7,9-12 OAc, which could correspond

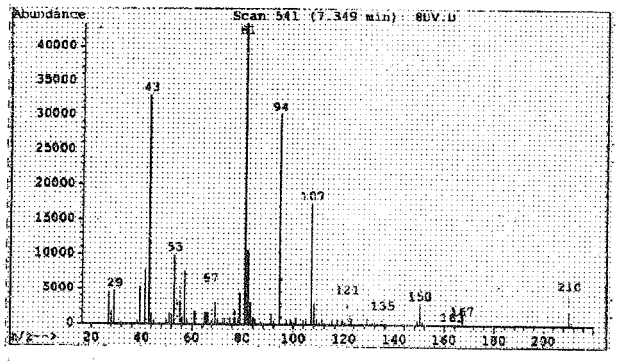
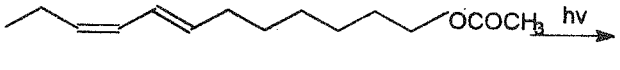


Fig. 12. The mass-spectrum of the component with the retention time of 7.35 min in Fig. 10

to two suplementary atoms of oxygen.

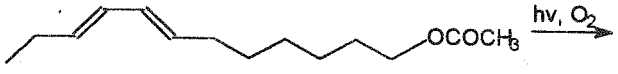
This component could be probably an peroxydic cycle, with an unsaturation. The reactions involved in degradation of (E,Z)-7,9-12 OAc, (1), as described by SHANI & KLUG (1980a) can be confirmed. The cyclic peroxide is reported also by IDESES et al. (1982b), as an isolable intermediate in singlet oxygen oxidation of pheromone resulting in the furan system. This could explain the ion m/z 113.

The molecular ion m/z 256 eliminates a neutral water molecule, resulting in the ion m/z 238.

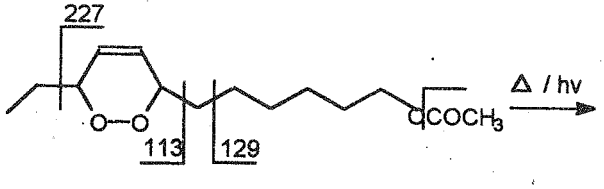


(1)

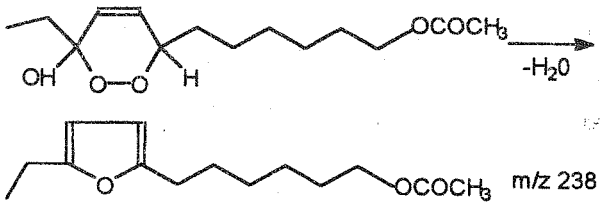
(E,Z)



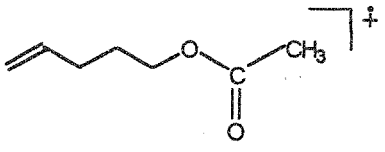
(E,E)



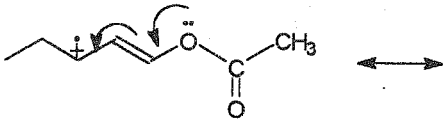
M=256



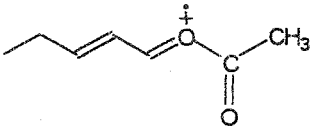
The ion m/z 128 has probably been formed from the ion m/z 129 by the scission of a hydrogen radical, with the structure *(a)* or more probably *(b)*, stabilized by resonance.



a, m/z 128



b, m/z 128



The ions m/z 61 and m/z 43 (the main peak) support the acetate structure.

The ion m/z 167 (M-acetic acid and ethyl radical) could eliminate two neutral molecules with mass 28 (probably ethene) resulting in the ions m/z 139 and m/z 111 (Fig. 14).

The ion m/z 113 elimates a neutral molecule of ethene, resulting in the ion 85 (113-28=85), which can also lose a neutral molecule with mass 28, resulting the ion m/z 57. The ions m/z 57 and 85 superpose the ions C_nH_{2n+1}, which could explain the high intensity of these ions.

In the acetone extract (Fig. 11), other degradation products can be found.

The mass-spectrum of the peak with the retention time 6.22 min (Fig. 11) presented in Fig. 15, is compared to that of the 3-hydroxy-cyclohexanone, suggested by the Spectrum Library Wiley 275 as the most probable spectrum.

Hydroxy-cyclohexanone has the molecular ion m/z 114. The ion m/z 96 is obtained by the elimination of a neutral molecule of water (114-96=18). The ion m/z 86 is obtained by the scission of a neutral molecule of carbon monoxid from the molecular ion (114-

86=28). The scission of the both parts releases the ion m/z 68 (114-68=46=28+18).

The last ion appears in the mass-spectrum of the peak with a retention time 6.22 min at m/z 168 and it is 54 mass units bigger than the hydroxy-

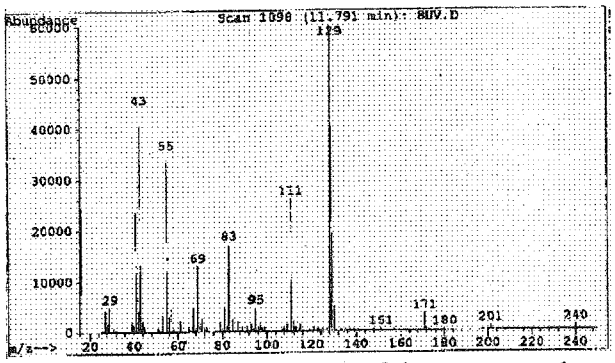


Fig. 13. The mass-spectrum of the compound with the retention time of 11,79 min in Fig. 10

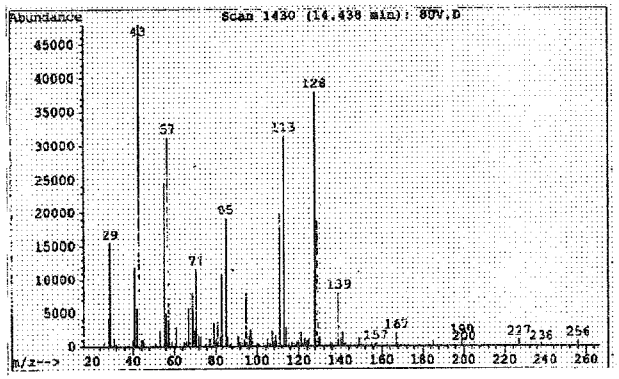
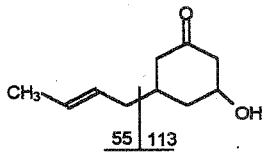


Fig. 14. The mass-spectrum of the compound with the retention time of 14,44 min in Fig. 10

cyclohexanone. This would correspond to an alkylic chain with three carbons, an oxygen and two double bonds or four carbons containing one double bond, which could justify the ion m/z 55, the second largest peak in the spectrum.



M=168

The mass-spectrum of the component with the retention time of 7,68 min (Fig. 11) is presented in Fig. 16, together with the 3-octenol acetate proposed by the software, as having a higher similarity to the searched degradation product (M=170).

The ions m/z 127 (M-43), m/z 110 (M-60), m/z 60 and m/z 61 point to the acetate structure.

According to the mass-spectra of the peaks 7.68 and 7.50 min (Fig. 11), these two compounds could be isomers.

According to previous searches, furanic degradation products and cyclic peroxyde have also been identified in this work. They have been described by means of NMR (SHANI & KLUG 1980A, IDESES ET AL. 1982B). This work brings further mass-spectrum information.

Besides these degradation products a series of acetates with chain lengths different from the one of the intitial dodecadienyl acetate was formed (8, 10, 11 and 18 carbon atoms). Also in several cases a double bond was absent. The high stability of the acetate group present in allmost all the degradation products is obvious.

Fig. 2. shows a decrease of the concentration to zero after 60 min in a straight line, which suggests

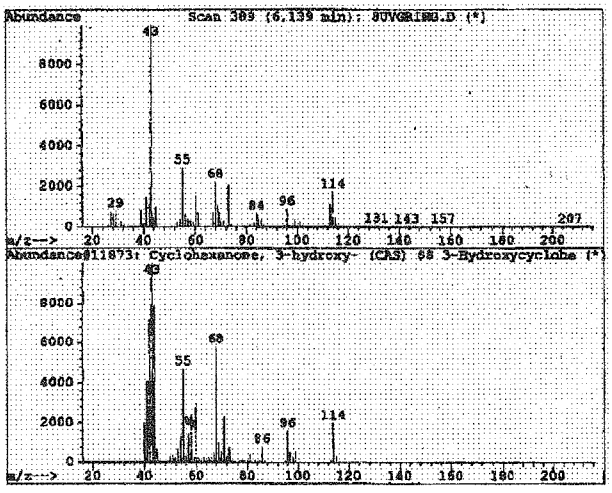


Fig. 15. Comparison of spectra of the compound with retention time 6.22 min (Fig. 11) and that of the 3-hydroxy-cyclohexanone

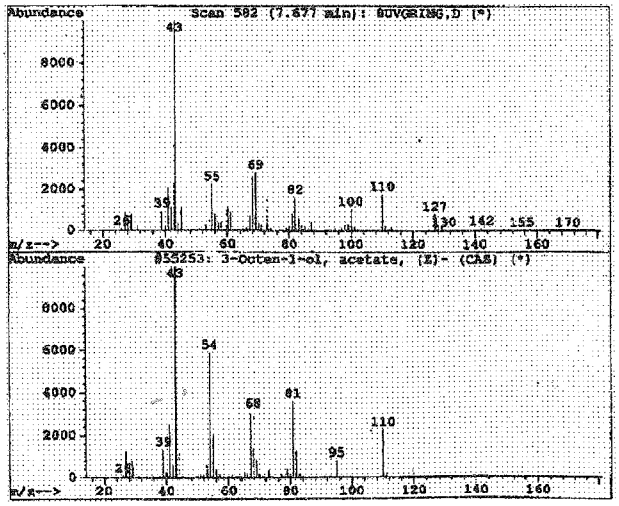


Fig. 16. Comparison of spectra of the compound with retention time 7.68 min (Fig. 11) and that of the 3-octenol acetate

first order kinetics according to the results reported by PANADES et al. (1998).

During all field experiments grape moths *Lobesia botrana* were present in the vineyard. After the experimental period of 29 days, 92 specimens *Lobesia botrana* were caught in the adhesive traps containing baits with the fresh pheromone. The traps containing the pheromone pre-exposed to UV light (hexane extract) did not capture insects of this species, the concentration of the pheromone after 21 hours being zero. Surprisingly, insects of other species have been captured, as presented in Tab. 2.

Table 2.

Insects captured in traps, using the *Lobesia botrana* pheromone modified by UV irradiation

Nr.	Species	Nr. of the captured insects
1.	*Cydia pomonella*	61
2.	*Lymantria dispar*	13
3.	other casual species	21

One may rise the question of whether the insects belonging to the two other species have been attracted by degradation products of the *Lobesia botrana* pheromone. For our analysis we can exclude that this pheromone turned into a pheromone component of the attracted species, or in one of its isomers.

In the case of *Lymantria dispar*, the 13 moths have been captured on two of 16 adhesive surfaces (11+2 insects). If initially a female moth of this species would have been caught by the trap, the attraction of further males would be easily explained. However all of the 13 specimens captured were males.

Likewise, in the case of *Cydia pomonella*, all of the 61 insects captured by 10 adhesive surfaces were males. Electrophysiological investigations are planned in order to investigate possible effects of degradation products on antennal olfactory receptor cells of *Cydia pomonella*.

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