DETERMINATION OF THE ACTIVE AGENT CONTENT IN PESTICIDES BY IR AND UV SPECTROPHOTOMETRY

Determination of 8-*dodecene*-1-*ol acetate* (Z) *and* 8,10-*dodecadiene*-1-*ol* (*E*,*E*)

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Summary

Methods for quantitative determination of two sex pheromones, applicable in the analysis of plant protection products were developed. 8-Dodecene-1-ol acetate (Z) was determined by IR spectrophotometry at 1740 cm^{-1} in carbon tetrachloride solution. 8,10-Dodecadiene-1-ol (E,E) was determined by UV spectrophotometry at 34.385 cm^{-1} in ethanolic solution.

In this paper we report two spectrophotometric methods developed for determining two insect sex pheromones used in plant protection: 8-dodecene-1-ol acetate (Z) and 8,10-dodecadiene-1-ol (E,E). The methods do not require previous separation of the components in the product.

The pheromones are used in plant protection by applying them, after addition of an antioxidant, on the surface of rubber capsules which are then placed into adhesive-coated containers; these containers are exposed in the areas to be protected. From the number of insects captured on the capsule one can conclude on optimum time for spraying. Another mode of application consists in deranging the copulation of the insects by keeping pheromone concentration above a defined threshold value; damage caused by the insects will then decrease by reason of progeny reduction.

The advantage of pheromones in plant protection is that it kills insects discriminatively; useful insects will not be destroyed.

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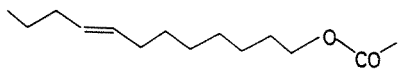
Literature review

8-Dodecene-1-ol acetate (Z) is the sex pheromone of Grapholita molesta, an apple orchard pest; it was first isolated by Roelofs et al. [2] in 1969.

The chemical structure of the compound is

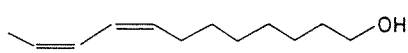


Later other researchers also isolated this compounds [56, 57, 65] and many authors identified its structure [41, 43, 46, 63, 83, 85, 88, 89].

Its biological effect was first studied by Baker et al. [69], subsequently by many others [30, 31, 35, 36, 38, 40, 41, 44, 47, 48, 52, 53, 58, 59, 60, 61, 65, 67, 69, 71, 73, 79, 80, 83, 85]. It was found that the pheromone synthetized by the insect is a mixture of four isomers in a fixed proportion. Their synthesis was studied first by Kovaleva et al. [2, 32, 33, 37, 39, 45, 52, 54, 55, 62, 63, 64, 68, 70, 72, 74, 75, 77, 78, 79, 81, 82]. Numerous researchers were engaged in their stereospecific synthesis [2, 7, 29, 34, 42, 47, 49, 50, 51, 52, 67, 73, 76] and determined the isomer proportion most efficient from the view of biological effect.

Only few data are found in the literature on the analysis of the compound [52, 56, 65, 66], limited to gas chromatography and mass spectroscopy.

8,10-*Dodecadiene*-1-*ol* (*E*,*E*) is the sex pheromone of another apple orchard pest: Laypeyresia pomonella. Its structure is



The compound was isolated by Roelofs et al. [1] in 1971; they also determined its structure.

The biological activity of its isomers was studied by numerous researchers [8, 14, 15, 19, 23, 27, 28, 84, 88]. Its synthesis has been described in many papers [1, 3, 4, 6, 10, 12, 13, 16, 17, 20, 21, 22, 25, 26, 86, 87].

Stereospecific synthesis of the compound was developed by Henrich et al. [25].

Its biological activity under natural conditions was studied by many researchers [4, 5, 6, 7, 11, 24].

Only two literature references were found regarding its analytical determination [9, 18]. Gas chromatography and mass spectrometry are again the methods applied.

Up to the present nobody reported their spectrophotometric investigation, and the spectra are not contained in the best-known spectra collections [91, 92, 93, 94, 95, 96].

In recent years the cited two pheromones are being applied as active agents in industrial products. It therefore became necessary to develop simple, rapid analytical methods not requiring their separation.

Experimental

For IR spectrophotometry, a Zeiss UR 10 spectrophotometer was used. The samples were dissolved in carbon tetrachloride; 1 mm layer thickness cuvettes with sodium chloride windows were applied. The spectrum of the active agent was recorded in a 0.02 mm cuvette.

UV spectrophotometric measurements were performed with a Zeiss Specord UV-VIX instrument, in 1 cm quartz cuvettes, using ethanolic solutions.

Results and discussion

Quantitative determination of 8-*dodecen*-1-*ol acetate* (*Z*)

We first separately recorded the IR spectra of the components, that is, of the active agent, the antioxidant and the solvent Fig. 1, 2.

The interpretation of the adsorption bands of the active agent is summarized in Table 1.

A comparision of the IR spectra of the active agent and the antioxidant demonstrates that in the interval around 1740 cm^{-1} the active agent has an intense absorption band, while the absorption of the antioxidant is only background-type. Hence the concentration of the active agent should be determinable without previous separation from the antioxidant by means of the absorbance measured in this interval.

For calibration a series of samples was prepared taking into account the expected composition of the samples (Table 2). From the absorbance results of several parallel measurements for each concentration we calculated the equation of the calibration line by means of the least squares approach:

$$A = 0.54 + 0.147\ c\ .$$

Since the determination is carried out after dissolution of the product from the rubber capsule with carbon tetrachloride, we investigated what

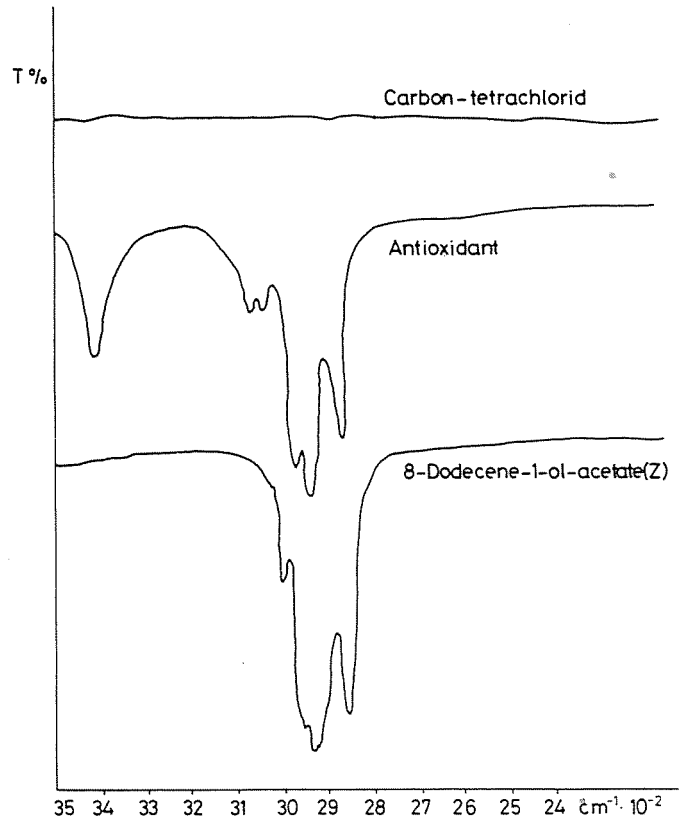


Fig. 1. IR spectra of sex pheromone product components and solvent applied in the 3500–2400 cm^{-1} range

carbon tetrachloride dissolves from the material of an empty capsule under identical conditions with those applied for preparation of the samples. The spectrum of the dissolved matter is represented by Fig. 3. From the absorption bands we stated that it is ethylene-ethyl acrylate copolymer.

For the actual determination of the active agent content, we dissolved the product from 10 capsules and evaporated the solution to 10 cm^3, i.e. to the volume used in calibration. To compensate the matrix effect, we placed an equal volume of carbon tetrachloride used for extraction of 10 empty capsules into the path of the IR beam. From the absorbance values measured, we estimated the active agent concentration by means of the calibration line. We found that the capsules contain—in average—1.1 mg active agent. The 99% confidence interval was 1.1 ± 0.04 mg. The concentration interval calibrated

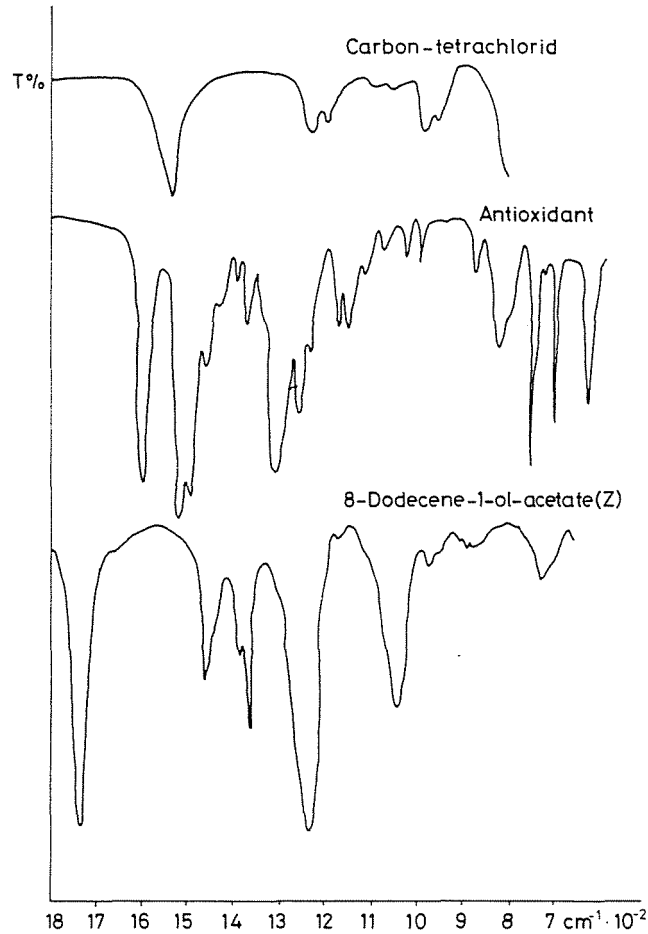


Fig. 2. IR spectra of sex pheromone product components and solvent applied in the 1800–700 cm^{-1} range

was 1 to 7 mg/cm^3, the slope of the calibration line was 0.147 $(mg/cm^3)^{-1}$. The purity of the substance used for calibration was 99%.

By determining the dependence of absorbance on dissolution time we found that 1 hour is required to obtain quantitative dissolution.

Quantitative determination of 8,10-*dodecadiene*-1-*ol* (*E*,*E*)

Since this compound is more volatile than 8-dodecene-1-ol acetate (Z), evaporation after dissolution from the capsules would lead to losses. For this reason, IR spectrophotometry requiring more concentrated solutions could

Table 1

Assignement of IR absorption bands of 8-dodecene-1-ol acetate (Z) to structure

Absorption bands, cm^{-1}	Interpretation
3000	ν (=CH)
2955	ν_{as} (CH_3)
2925	ν_{as} (CH_2)
2850	ν_s (CH_3); ν_s (CH_2)
1740	ν (C=O) (ester)
1655 (weak)	ν (C=C) (trans)
1467	β_s (CH_2)
1455	δ_{as} (CH_3); β_s (CH_2) (beside unsaturatedness)
1440	δ_{as} (CH_3) (ester); β_s (CH_2) (beside unsaturatedness)
1390	δ_s (CH_3)
1367	δ_s (CH_3) (ester)
1240	ν_{as} (C—O—C) (ester)
1045	ν_s (C—O—C) (ester)
975	γ (=CH) (trans)
895	—
880	—
860	—
750 (Weak)	γ (=CH) (cis)
727	β_{as} (CH_2)
630	—

Remark: ν valence vibration; β, γ, δ deformation vibration; subscripts *s*, *as*: symmetric and asymmetric vibration, resp. [90]

Table 2

Data of calibration series for 8-dodecene-1-ol acetate (Z)

Component	Serial number						
	1	2	3	4	5	6	7
8-dodecene-1-ol acetate (Z) (mg/cm^3 CCl_4)	6.7	5.0	3.4	2.5	1.25	0.625	0.156
Antioxidant (mg/cm^3 CCl_4)	0.67	0.50	0.34	0.25	0.12	0.063	0.016

not be used for determination of this pheromone; we therefore chose UV spectrophotometry. UV spectra were already recorded by the authors of [1] and [97], but they did not report data.

The indivudual UV spectra of the active agent and the antioxidant (Fig. 4) demonstrated that in the region of 34.385 cm^{-1} the absorbance of the antioxidant is background-type only, and hence this absorption band is suited for quantitative determination of the active agent without previous separation.

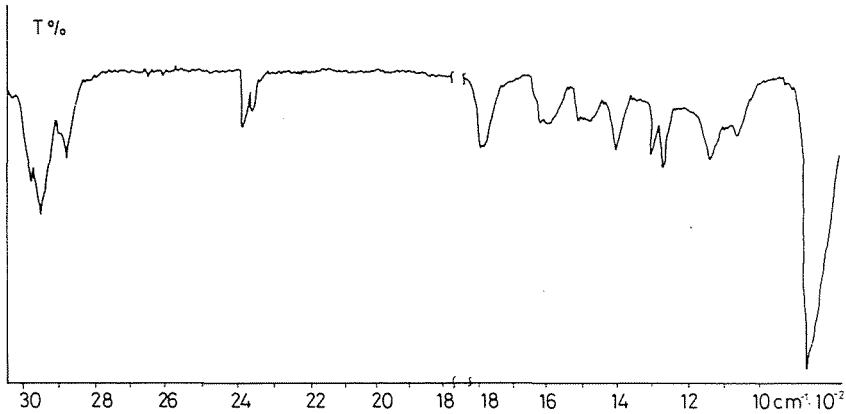


Fig. 3. IR spectrum of the carbon tetrachloride extract of empty capsules

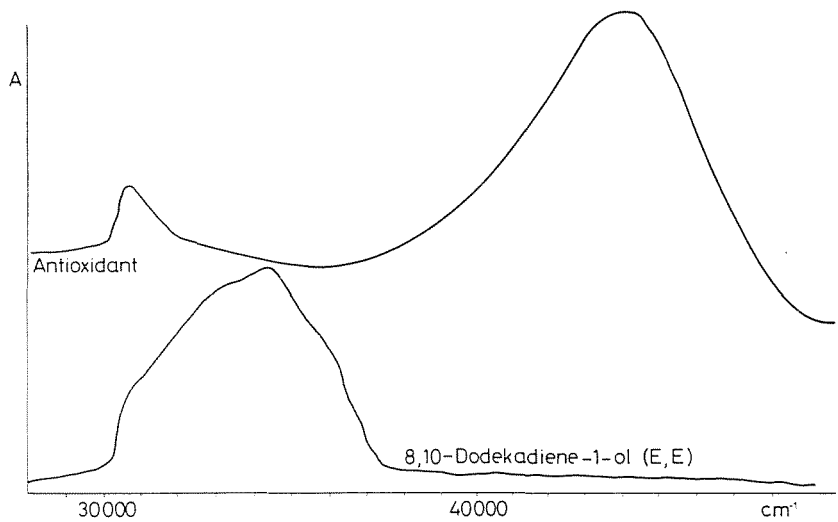


Fig. 4. UV spectra of sex pheromone product components

Calibration data are listed in Table 3. The equation of the calibration line is

$$A = 0.014 + 0.25\ c\,.$$

We used 10 cm^3 ethanol to dissolve the active agent and the antioxidant from one capsule. Previously we determined how much time is required for quantitative dissolution and found that this is close to 3 hours (Fig. 5). This being rather long, is appeared reasonable to investigate the stability of the

Table 3

Calibration data for 8,10-dodecadiene-1-ol (E,E)

Component	1	2	3	4	5
8,10-dodecadiene-1-ol (E,E) ($\mu g/cm^3$ ethanol)	6.87	13.75	20.12	27.50	41.25
Antioxidant ($\mu g/cm^3$ ethanol)	0.68	1.37	2.01	2.75	4.12

active agent's solution. We found, however, that no appreciable absorbance change occurs during 24 hours.

Analysis of the samples was performed similarly to IR measurements; here also we placed a solution obtained under identical conditions from an empty capsule into the path of the beam to eliminate the interfering effect of matter dissolved from the material of the capsule.

The concentration estimated by means of the calibration line was 30 μg active agent per capsule. Calibration covered the concentration range of 5 to 40 $\mu g/cm^3$, sensitivity was 0.25 $(\mu g/cm^3)^{-1}$.

The 99% confidence interval was 30 ± 0.3 μg per capsule.

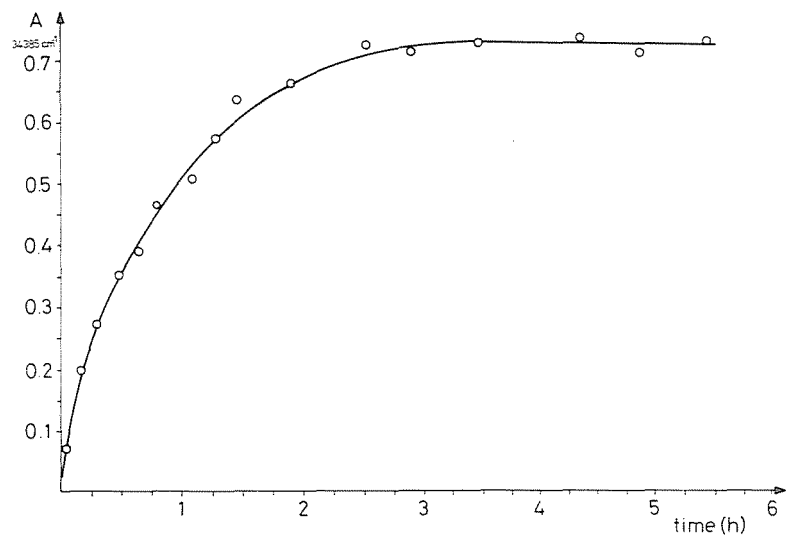


Fig. 5. Absorbance of 8,10-dodecadiene-1-ol at 34.485 cm^{-1} *vs.* dissolution time

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