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SYNTHESIS OF DODEC-10E-ENYL ACETATE — THE SEX PHEROMONE OF *Phyllonorycter blancardella* (LEPIDOPTERA: GRACILLARIIDAE)

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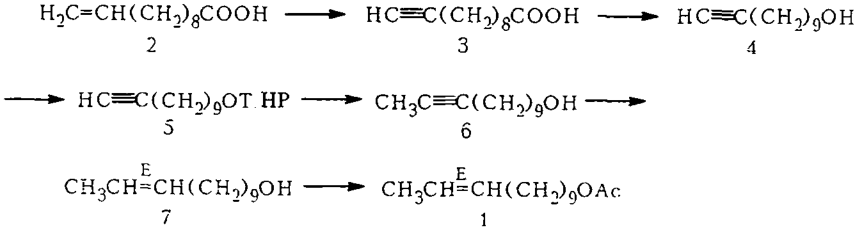
Dodec-10E-enyl acetate has been synthesized from undecenoic acid. Field trials have shown its high attractiveness for Phyllonorycter blancardella *males.*

The apple leaf miner moth *Phyllonorycter blancardella* (Lepidoptera: Gracillariidae) — a dangerous pest of fruit crops — is widely distributed in Moldova and the southern regions of the Ukraine and Russia [1]. The sex pheromone of *Ph. blancardella* includes dodec-10E-enyl acetate [2, 3].

Dodec-10E-enol and its acetate (1) have been detected in a natural extract of the pheromone of the pea moth *Laspeyresia negricana* [4]. Syntheses of the acetate (1) by the stereoselective reduction of diethyl γ-alkyl-substituted allylphosphonates with $LiAlH_4$ [4], through acetylenic intermediates [5], by the use of the Wittig reaction [6], and by the alkylation of crotyl acetate in the presence of Li_2CuCl_4 [7] have been described.

In the present paper we consider a method of synthesizing the acetate (1) from undecenoic acid:



$$\underset{2}{H_2C{=}CH(CH_2)_8COOH} \longrightarrow \underset{3}{HC{\equiv}C(CH_2)_8COOH} \longrightarrow \underset{4}{HC{\equiv}C(CH_2)_9OH}$$

$$\longrightarrow \underset{5}{HC{\equiv}C(CH_2)_9OTHP} \longrightarrow \underset{6}{CH_3C{\equiv}C(CH_2)_9OH} \longrightarrow$$

$$\underset{7}{CH_3CH\overset{E}{=}CH(CH_2)_9OH} \longrightarrow \underset{1}{CH_3CH\overset{E}{=}CH(CH_2)_9OAc}$$

Undecenoic acid (2) was converted into undecynoic acid (3) with a yield of 85.5% by bromination with bromine followed by the splitting out of HBr with sodium in liquid ammonia. The undecynoic acid was converted into 1-(tetrahydropyran-2-yloxy)undec-10-yne (5) by reduction with $LiAlH_4$ followed by protection of the OH group of the resulting alcohol (4) with dihydropyran. Compound (5) was alkylated with CH_3I in the presence of $LiNH_2$ in liquid ammonia. Reduction of the alcohol (6) in diglyme at 150°C gave the alcohol (7), and acetylation of the latter formed the desired acetate (1).

Field trials of the acetate (1) showed its high biological activity for *Phyllonorycter blancardella* males. The results of the trials are given in Table 1.

EXPERIMENTAL

IR spectra of solutions of the substances in CCl_4 were taken on an IR-75 instrument using a NaCl cell with a layer thickness of 0.125 μm. PMR spectra of solutions of the substances in CCl_4 were obtained on a BS-467A spectrometer with a working frequency of 60 MHz, using HMDS as standard. The purity of the substance obtained and the completeness of reduction were monitored by GLC on a Chrom-5 instrument with a glass column (3 mm × 2.5 m) containing 5% of the phase SE-30 on Chromaton, 60-80 mesh. The results of analysis of the compounds obtained corresponded to the calculated figures.

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TABLE 1. Result of the Trapping of Apple Leaf Miner Moth Males for Various Doses of the Pheromone (Moldova, village of Stavcheny)

Dose, μg	Males trapped according to the records from July 2, 1993, to August 23, 1993										
	1	2	3	4	5	6	7	8	9	Sum Y	X
100	1750	670	280	1580	2100	3500	2890	1050	450	14270	528
500	1820	560	130	1220	1898	4670	2750	940	500	14488	536.5
1000	1250	430	189	890	2000	3560	3150	820	580	12869	476.6
Sum R	4820	1660	599	3690	5998	11730	8790	2810	1580	41627	1541.7

Undec-10-ynoic Acid (3). At −20°C, 33.6 g (0.21 mole) of bromine was added to a solution of 36.84 g (0.20 mole) of undec-10-enoic acid in 200 ml of abs. diethyl ether. The resulting solution was added over 30 min to a suspension of 1.0 g-atom of sodium in liquid ammonia. After all the solution had been added, part of the ammonia was driven off, and 53.5 g of NH_4Cl was added to the reaction mixture, which was then left overnight. The deposit was dissolved in water and neutralized with dilute HCl. The organic layer was separated off, and the aqueous layer was extracted to exhaustion with diethyl ether (2 × 50 ml). The ethereal extracts were washed with water, dried with Na_2SO_4, and evaporated. This gave 32 g (85.5%) of the acid (**3**) with mp 41-42°C.

Undec-10-ynol (4). With stirring and cooling, 30 g (0.16 mole) of the acid (**3**) was added to a suspension of 5.7 g (0.15 mole) of $LiAlH_4$ in 200 ml of abs. diethyl ether. After addition was complete, the reaction mixture was heated at 40°C for 3 h and it was then cooled, carefully decomposed with water, and extracted with ether. The ethereal extract was dried and evaporated, and vacuum distillation then gave 23.5 g (85%) of the alcohol (**4**), bp 125-127°C (2 mm), n_D^{20} 1.4550. IR spectrum (ν, cm^{-1}): 2100 (C=C), 3280, 3640 (C—OH).

Dodec-10-ynol (6). With stirring and cooling, 10.9 g (0.13 mole) of freshly redistilled dihydropyran was added to 20 g (0.12 mole) of the alcohol (**4**) containing a few drops of concentrated HCl. The reaction mixture was stirred at 20°C for 3 h and was neutralized with Na_2CO_3. The resulting compound (**5**) was added dropwise to a suspension of $LiNH_2$ in liquid ammonia (1.6 g [0.23 g-atom] of Li and 150 ml of NH_3). After an hour, a fivefold excess of CH_3I in 100 ml of abs. THF was added to the reaction mixture. Stirring was continued for 3 h, the ammonia was evaporated off, and the residue was decomposed with a saturated solution of NH_4Cl and extracted with diethyl ether (3 × 50 ml). The solvent was driven off, and the residue was hydrolyzed with 30 ml of 16% H_2SO_4 in 300 ml of ethyl alcohol at 50°C for an hour. This gave 20 g (92%) of the alcohol (**6**), with bp 125-128°C (2 mm), n_D^{20} 1.4622. IR spectrum (ν, cm^{-1}) 2100 (C=C), 3640 (C—OH).

Dodec-10-enol (7). A mixture of 10 ml of abs. THF, 80 ml of diglyme, and 5 g (0.13 mole) of $LiAlH_4$ was heated with stirring in a current of nitrogen, and the low-boiling fraction was distilled off. The resulting suspension was treated slowly, at 10°C, with 8 g (0.04 mole) of (**6**) in 10 ml of diglyme. The temperature of the reaction mixture was raised to 140°C and stirring was continued for 48 h. The reaction mixture was cooled and was hydrolyzed with ice water in an atmosphere of nitrogen. The precipitate was filtered off, the solution was washed three times with pentane, and the resulting extract was dried with $MgSO_4$. The solvent was evaporated off, and the residue was distilled in vacuum. This gave 7.6 g (95%) of the alcohol (**7**) with bp 113-115° (2 mm), n_D^{20} 1.4545. IR spectrum (ν, cm^{-1}) 960, 1050 (C=C), 2920, 3600 (C−OH). PMR spectrum (ppm): 0.93 (3H, CH_3, t), 1.2-1.8 (8H, CH_2C=C, m), 3.6 (2H, CH_2OH, s), 5.4 (2H, C=C, m).

Dodec-10E-enyl Acetate (1). A mixture of 7.3 g (0.04 mole) of the alcohol (**7**) and 10.2 g (0.14 mole) of pyridine in 50 ml of abs. diethyl ether and 11 g (0.14 mole) of AcCl yielded 7.3 g of the acetate (**1**), bp 112-113° (2 mm), n_D^{20} 1.4446. IR spectrum (ν, cm^{-1}): 965 (CH=CH), 1730 (C=O). PMR spectrum (ppm): 0.90 (3H, CH_3, m), 1.3-1.75 (9H, CH_2, m), 2.00 (4H, CH_2C=C, m), 4.07 (2H, CH_2O), 5.1-5.4 (2H, CH=CH).

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