# SYNTHESIS OF (E)-DODEC-3-EN-1-YL ACETATE – THE MAIN COMPONENT OF SEX PHEROMONES OF Scrobipalpa ocellatella AND Scrobipalpopsis solanivora

L. M. Bikulova, G. G. Verba,
F. G. Kamaev, and A. A. Abduvakhabov

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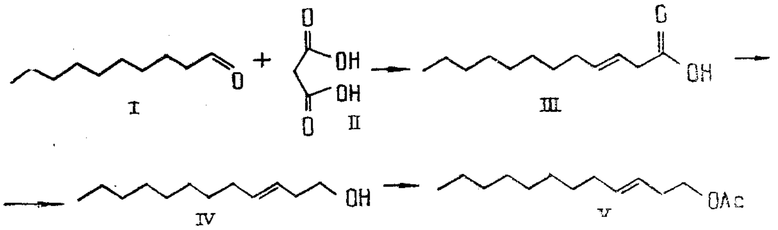
(E)-Dodec-3-en-1-yl acetate – the main component of the sex pheromones of Scrobipalpa ocellatella and Scrobipalpopsis solanivora – has been obtained by a three-stage synthesis from decanal and malonic acid. The overall yield of pheromone was 33% calculated on the initial aldehyde.

(E)-Dodec-3-en-1-yl acetate has been isolated and identified as the main component of the sex pheromones of the beet-mining moth Scrobipalpa ocellatella [1] and the potato moth Scrobipalposis solanivora [2]. Syntheses of these compounds based on the β-oxyethylation of dec-1-yne with ethylene oxide have been described [1, 3].

We have developed a convenient synthesis of (E)-dodec-3-en-yl acetate (V) which is based on a modified [4] Knoevenagel condensation between the readily available decanal (I) and malonic acid (II). This gave a good yield of the key synthon – (E)-dodec-3-enoic acid (III), which was reduced with lithium tetrahydroaluminate to (E) dodec-3-en-1-ol (IV). Acetylation of the alkenol (IV) led to the desired product (V).



The overall yield of the pheromone (V) in the three-stage synthesis amounted to 33%, calculated on the initial aldehyde (I). According to the results of GLC analysis, the chemical purity of the product was not less than 97%. The trans configuration of the pheromone obtained was confirmed by the presence of characteristic IR absorption in the 970 $cm^{-1}$ region and by the value of the spin-spin coupling constant of the olefinic protons in the PMR spectra of (IV) and (V) determined from double-resonance experiments. Its value, J = 15.0 Hz, corresponds to the trans-geometric isomerism of olefinic compounds [5].

## EXPERIMENTAL

IR spectra were taken on a Specord 71 IR spectrometer in $CCl_4$, and PMR spectra on a Varian XL-200 spectrometer with a working frequency of 200 MHz. The specimens used were 5% solutions of the substance under investigation in $CCl_4$. The chemical shifts are in the δ-scale relative to the signal of HMDS as internal standard. GLC analysis was performed on a Chrom-5 instrument with 5% of the silicone liquid SE-30 on Chromaton N-AW-DMCS as the stationary phase at a column temperature of 180°C with the carrier gas helium in a 3500 × 3 mm column.

(E)-Dodec-3-enoic Acid (III). A mixture of 15.6 g (0.15 mole) of malonic acid, 7.8 g (0.05 mole) of decanal, and 4.25 mg (0.05 mmole) of piperidine in 40 ml of p-xylene was boiled until the separation of water in a Dean-Stark trap ceased (4 h). The solution was

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A. S. Sadykov Institute of Bioorganic Chemistry, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 682-683, September-October, 1988. Original article submitted April 12, 1988.

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washed twice with water and was dried with $MgSO_4$. After evaporation and distillation, 7.0 g (70%) of the (E)-acid (III) was obtained. bp 155-158°C/3 mm; $n_D^{20}$ 1.4552.

IR spectrum (ν, $cm^{-1}$): 970 (trans-C=C) 1720 (CO). PMR spectrum (δ, ppm): 0,83 (3H, t, $CH_3$, J=6,0 Hz), 1,04—1,41 (12H, m, $CH_2$), 1,98 (2H, m, $C=CCH_2$), 2,96 (2H, d, $CH_2$—CO, J=6,1 Hz), 5,33—5,61 (2H, m, CH=CH).

(E)-Dodec-3-en-1-ol (IV). To a suspension of 1.44 g (0.038 mole) of lithium tetrahydroaluminate in 150 ml of absolute ether was added, dropwise, 6.3 g (0.032 mole) of (E)-dodec-3-enoic acid (III) in 15 ml of absolute ether at such a rate that the reaction mixture boiled gently. After the end of the addition of the (III), the mixture was stirred for another 3 h with heating. The excess of lithium tetrahydroaluminate was decomposed by the careful addition of water. The resulting precipitate was filtered off and was washed with ether (50 ml). The ethereal solution was dried with $MgSO_4$ and the solvent was evaporated off. This gave 3.5 g (60%) of the alcohol (IV), $n_D^{20}$ 1.4542 (see [3]).

IR spectrum (ν, $cm^{-1}$); 970, (trans-C=C); 3450 (OH). PMR spectrum (δ, ppm): 0,85 (3H, t, $CH_3$, J=6,0 Hz), 1,04—1,31 (12H, m, $CH_2$). 1,88—2,22 (4H, m, $C=CCH_2$), 3,48 (2H, t, $OCH_2$, J=6,3 Hz), 5,16—5,54 (2H, m, CH=CH, J=15,0 Hz).

(E)-Dodec-3-en-1-yl Acetate (V). A mixture of 1.67 g (0.009 mole) of (E)-dodec-3-en-1-ol (IV), 5.8 ml of acetic anhydride, and 5.8 ml of pyridine was stirred at room temperature for 36 h. By the usual treatment, the acetate (V) was obtained, its yield after chromatography on silica gel L 100/250 (60 g) (hexane—diethyl ether (3:1)) being 1.6 g (78.6%); $n_D^{20}$ 1.4490. Its IR spectrum was identical with that described in the literature [3]. PMR spectrum (δ, ppm): 0,84 (3H, t, $CH_3$); 1,10—1,34 (12H, m, $CH_2$), 1,93 (3H, s, $CH_3CO$), 1,86—2,28 (4H, m, $C=CCH_2$), 3,94 (2H, t, $CH_2O$, J=6,3 Hz), 5,16—5,50 (2H, m, CH=CH, J=15,0 Hz).

## SUMMARY

The synthesis of (E)-dodec-3-en-1-yl acetate – the main component of the sex pheromones of the beet mining moth *Scrobipalpa ocellatella* and the potato moth *Scrobipalpopsis solanivora* – has been effected with the aid of the Knoevenagel condensation.

## LITERATURE CITED

1. M. Renou, C. Descoins, J. Y. Lallemand, E. Priesner, M. Lettere, and M. Gallois, Z. Angew. Entomol., 90, 275 (1980).
2. B. F. Nesbitt, P. S. Beevor, A. Cork, D. R. Hall, R. M. Murillo, and H. R. Leal, Entomol. Exp. Appl., 38, 81 (1985).
3. L. Pop, I. Oprean, A. Barabas, and F. Hodosan, J. Prakt. Chem., 328, 867 (1986).
4. N. Ragoussis, Tetrahedron Lett., 28, 93 (1987).
5. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution NMR Spectroscopy, Vol. II, Pergamon, Oxford (1966).