

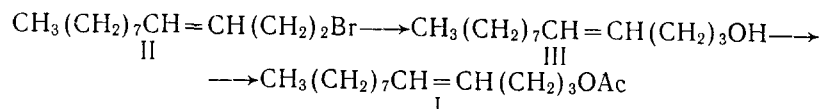
SYNTHESIS OF TRIDEC-4-EN-1-YL ACETATE - THE SEX PHEROMONE
OF *Keiferia lycopersicella*

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The sex pheromone of a dangerous pest of vegetable crops (the tomato pinworm *Keiferia lycopersicella* (Wals.)) is tridec-4-en-1-yl acetate (I) [1-3]. A method for the synthesis of attractant (I) has been described as the key stage of which was the transformation of an alk-5Z-en-4-olide into an alk-4E-enoic acid [4].

We have performed a two-stage synthesis of the acetate (I), starting from the readily available 1-bromododec-3E-ene (II), which has been used previously in the synthesis of an imitator of the pheromone of a moth *Rhynchopacha* sp. [5].



The interaction of the Grignard reagent generated from the bromide (II) with paraformaldehyde, as described in [6], gave, after chromatography on SiO₂ (ether-hexane (1:1) tridec-4E-en-1-ol) (III) with a yield of 31.8%. IR spectrum (ν , cm⁻¹): 970 (trans-CH=CH), 3380 (OH). PMR spectrum (200 Mhz, CHCl₃): 0.87 (3H, t, CH₃, J = 6.4 Hz), 1.22-1.42 (14H, br.s, CH₂), 1.90-2.10 (4H, m, C=CCH₂), 3.54 (2H, t, OCH₂, J = 7.2 Hz), 5.3-5.6 (2H, m, CH=CH, J = 15.2 Hz). Mass spectrum, m/z: 198 M⁺.

Acetylation of the alkenol (III) with acetic anhydride in pyridine gave the desired pheromone (I) with a yield of 86%, n_D^{30} 1.4385. According to the literature [4]: n_D^{22} 1.4440. IR spectrum (ν , cm⁻¹): 970 (trans-CH=CH), 1740 (CO). PMR spectrum (200 MHz, CHCl₃): 0.87 (3H, t, CH₃, J = 6.4 Hz), 1.20-1.42 (14H, br.s, CH₂), 1.98 (3H, s, COCH₃), 1.90-2.10 (4H, m, C=CCH₂), 3.54 (2H, t, OCH₂, J = 7.2 Hz), 5.28-5.58 (2H, m, CH=CH, J = 15.2 Hz). Mass spectrum, m/z: 180 (M⁺ - CH₃COOH).

LITERATURE CITED

1. R. A. Van Steenwyk, E. R. Oatman, and J. A. Wyman, *Econ. Entomol.*, **76**, 440 (1983).
2. W. B. Roelofs and L. Bjostad, *J. Biol. Chem.*, **12**, 279 (1984).
3. H. Arn, M. Toth, and E. Priesner, *List of Sex Pheromones of Lepidoptera and Related Compounds*, IOBS-WPRS (1986), p. 17.
4. G. G. Melikyan, G. Kh. Aslanyan, K. A. Atanesyan, D. A. Mkrtchyan, and Sh. O. Badanyan, *Khim. Prir. Soedin.*, 106 (1990).
5. G. G. Verba, L. M. Bikulova, A. A. Abduvakhobov, and F. G. Kamaev, *Khim. Prir. Soedin.*, No. 1, 129 (1991).
6. L. I. Smith and L. J. Spillane, *J. Am. Chem. Soc.*, **62**, 2639 (1940).

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