Thus, it may be concluded that for the production of berberine it is desirable to gather the roots at the end of vegetation and the young shoots and leaves during the period of mass flowering.

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# SYNTHESIS OF THE PHERMONE OF Ephestia kuehniella

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The Mediterranean flour moth is one of the main pests of stored cereals. The pheromone of the Mediterranean flour moth is tetradeca-9Z,12E-dienol acetate (I). The presence of a methylene-separated diene system complicates the performance of a stereospecific synthesis. In the synthesis of aliphatic dienic pheromones the main methods are the elongation of the chain of an unsaturated fragment already having a double bond with the required configuration or a double and a triple bond, or the coupling of synthons each of which has an unsaturated bond (for example, [1-4]), but syntheses by the elongation of a fragment containing a 1,4-nonconjugated system are encountered considerably more rarely. In particular, we may mention the work of Bac and Langlois [5], who obtained 1-dimethylaminohepta-2Z,5E-diene by the stereoselective fragmentation of 1,2,3,6-tetrahydropyridine methiodide with cesium fluoride. Subsequently, these authors performed chain elongation with 1-chloro-7-(tetrahydropyran-2-yloxy)-heptane.

In the scheme for the synthesis of pheromone (I) that we propose, the main synthon – the enyne (2) – was obtained by the ethynylation of crotyl bromide:

$$\begin{gathered} CH_3-CH\overset{E}{=}CH-CH_2Br\rightarrow CH_3-CH\overset{E}{=}CH-CH_2-C\equiv CH\rightarrow \\ \xrightarrow[2.\ Ac_2O/AcOH]{1\ \ THP-O-(CH_2)_8Cl} CH_3-CH\overset{E}{=}CH-CH_2-C\equiv C- \\ -(CH_2)_8OCOCH_3\xrightarrow{H_2/P-2Ni} CH_3-CH\overset{E}{=}CH-CH_2- \\ -CH\overset{Z}{=}CH-(CH_2)_8OCOCH_3 \qquad (I) \end{gathered}$$

Ethnynylation was carried out in three ways: 1) by the interaction of the lithium acetylide–ethylenediamine complex with crotyl bromide in DMSO for 15 h; 2) by the interaction of crotyl bromide with lithium acetylide obtained by the dropwise addition of butyllithium (0.6 mole) to a saturated solution of acetylene in THF, with cooling (+5°C); and 3) via the Iotsich complex obtained in the following way: with cooling to –20°C, ethylmagnesium bromide was added to a saturated solution of acetylene in THF, and, after the addition of the whole amount, the mixture was stirred for 1 h while the temperature was allowed to rise to 0°C, and crotyl bromide was added, and then the reaction mixture was heated at 60°C for 1 h. In all cases, the reaction was stopped by the addition of water or ammonium chloride solution, the substance was extracted with ether, the extract was dried, the ether was evaporated off, and the residue was distilled in vacuum, bp 43-45°C/30 mm,

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$n_D^{20}$ 1.4670. The yield was 50-54%. The presence of the terminal triple bond was confirmed by IR and NMR spectroscopies. Consequently, all three methods are suitable for the ethynylation of crotyl bromide.

The action of lithium amide on hex-trans-4-en-1-yne gave the lithium derivative, the coupling of which with 1-chloro-8-(tetrahydropyran-12-yloxy)octane in hexametapol led to 1-(tetrahydropyran-2-yloxy)tetradec-trans-2-en-9-yne. The latter was acetylated without being isolated in the individual state. The yield of the acetate was 64%, bp 173-176°C/2mm, $n_D^{25}$ 1.4625. IR spectrum ($cm^{-1}$): 3000, 1725, 1230, 1030, 960, 715. PMR Spectrum; 5.2-5.7 (2H, m, $CH{=}CH$); 2.94 (2H, t, J = 5.8 Hz, $CH_2COO$); 2.72 (2H, m, $\equiv C{-}CH_2{-}C$); 2.08 (2H, m, $CH_2{-}C\equiv$); 1.93 (3H, s, $CH_3COO$); 1.63 (3H, dd, J = 6.0 Hz, 1.1 Hz, $CH_3{-}C{=}C$); 1.1-1.7 (12H, m, $CH_2$). Subsequent hydrogenation with P Ni catalyst gave tetradeca-cis-9,trans-12-dienyl acetate, the physicochemical constants and spectral characteristics of which agreed with those given in the literature [4]. Thus, a new route to the synthesis of the pheromone of the Mediterranean flour moth has been proposed.

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