

## Improved synthesis of (Z,E)-9,11,13-tetradecatrienal, the sex pheromone of the Carob Moth *Apomyelois* (= *Ectomyelois*) *ceratoniae* (Lepidoptera: Pyralidae)

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(Z,E)-9,11,13-Tetradecatrienal is a sex pheromone component emitted by virgin females of the Carob Moth *Apomyelois ceratoniae* Zeller (Lepidoptera: Pyralidae) which is an important pest of Iranian pomegranate fruits. Chemical control of this pest is not possible and biological methods with pheromones are used. The synthesis of the major component of the sex pheromone was achieved in fewer steps and with lower cost than previously. (Z,E)-9,11,13-Tetradecatrienal was synthesised by four steps with 59% overall yield. The coupling of a conjugated dienynol intermediate from E-1,2-dichloroethylene with vinyl magnesium bromide was achieved in good yield and followed by reduction of dienynol with activated zinc in THF-H<sub>2</sub>O and oxidation gave the aldehyde of the sex pheromone.

**Keywords:** synthesis, sex pheromone, stereoselective reduction

(Z,E)-9,11,13-Tetradecatrienal was isolated and synthesised by Millar (1990) as a component of the sex pheromone of the female Carob Moth, *Apomyelois ceratoniae*.<sup>1</sup> This insect is a worldwide pest of nuts and fruits including, in the United States, carobs, almonds, and dates. Moreover, in other parts of the world, this species is a primary pest of dates, almond and pistachio, and in Iran, an important pest of pomegranates.<sup>2,3,4</sup> Mining by larvae can damage the fruit introducing fungal saprophytes, rendering the fruit unacceptable for the fresh fruit market. Larvae remain protected for almost their entire development within the mines limiting the effectiveness of chemical control. There are many generations per year in different parts of Iran, and typically three to four generations can cause damage to fruit.<sup>5,6</sup> Insect pest management, monitoring and control programmes utilising sex pheromones as behaviour modifying chemicals have become necessary for several insect groups, particularly moths. Thus, a pheromone-based method for sampling *A. ceratoniae* populations by using traps to catch the adult male moths might provide a method for timing and so maximising the efficacy of control.

(8E,10E)-Tetradecadienal is a sex pheromone component of *Marmara gulosa* Guillén and Davis (Lepidoptera: Gracillariidae), which is a sporadic pest of citrus and a number of other crops. It was synthesised and used as a reliable and accurate tool for monitoring densities of *M. gulosa*.<sup>7</sup> The Z-isomer of the sex pheromone of the female Douglas Fir Cone Gall Midge, tridecadien-2-yl acetate with non-conjugated double bonds, was synthesised from a diyene by reduction over P-2 nickel in good yield. In Douglas Fir seed orchards, sticky traps baited with 2S-Z4-Z7 captured the male *Contarinia oregonensis* (Diptera: Cecidomyiidae).<sup>8</sup> Reduction of an alkyne stereoselectively to the *cis* or *trans* isomer is always a challenge in sex pheromone synthesis, and many reactions have been examined. In this regard, (Z,Z)-9,11-tetradecadienyl acetate, as a minor component of the sex pheromone gland of the Egyptian Cotton Leaf Worm, was stereoselectively reduced to the (Z,Z)-conjugated diene by Zn(Cu/Ag)/MeOH/H<sub>2</sub>.<sup>9</sup>

Three pheromone components including (Z,E)-9,11,13-tetradecatrienal, (Z,E)-9,11-tetradecadienal and (Z)-9-tetradecenol of *A. ceratoniae* were extracted by solvent. The first component, which was mentioned above, is quite active in attracting males in biological assays and field tests by itself.

The former major component has been synthesised in several steps.<sup>10,11</sup> Our synthesis of (Z,E)-9,11,13-tetradecatrienal improved the yield and removed two steps<sup>1</sup> which had limited its availability and were costly. We synthesised the major trienal aldehyde in a shorter route in which the conjugated double bonds (C9) were introduced with a high degree of stereochemical control (Fig. 1).

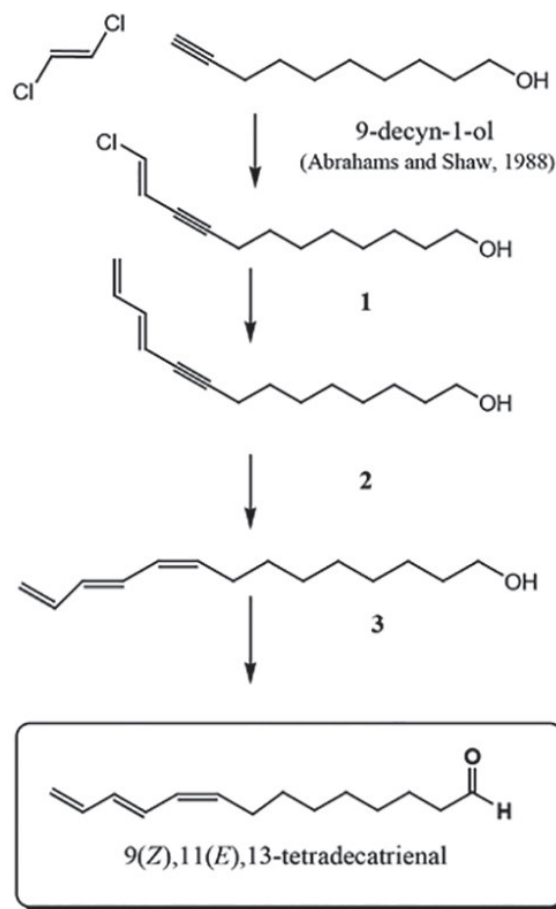


Fig. 1 Synthesis of (Z,E)-9,11,13-tetradecatrienal.

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