

LETTER ARTICLE

Stereospecific Synthesis of (4E,10Z)- 4,10-Tetradecadienyl Acetate, the Major Sex Pheromone of Apple Leaf Miner Moth, *Phyllonorycter ringoniella*

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Abstract: The main component of the sex pheromone of many lepidopteran pests, (4E,10Z)-4,10-tetradecadienyl acetate (1) has been synthesized stereoselectively by using a simple route with 4-pentynol as a starting material. The stereoselective formation of the 4E double bond is based on the stereospecific reduction of internal alkyne with lithium aluminium hydride (LAH) while Wittig reaction was used to achieve 10Z double bond in the target pheromone component. The GC purity of the final acetate was achieved 97.87% while isomeric purities are more than 99%. The green chemistry principle shows a new concept towards the multistep pheromone synthesis via green metrics calculations.

Keywords: Stereoselective synthesis, Apple leaf miner, *Phyllonorycter ringoniella*, Wittig olefination, Reduction, Gram scale synthesis, Green metrics calculations.

1. INTRODUCTION

An apple is one of the most widely cultivated fruit trees, which originated from central Asia and Europe and all around the world. An apple is regularly consumed because of its nutritional contents and rich phytochemicals; it has become an important fruit in the human diet. An apple is full of antioxidants, anti-proliferative and cell signaling effects. The consumption of an apple and apple juice/products may reduce the risk of chronic diseases. Also, beneficial effects on risks of Alzheimer's disease, asthma, cancer, as well as, cardiovascular diseases and diabetes [1,2]. All around the world, the apple orchards are mostly infested by various insect pests like apple leafminer moth (*Phyllonorycter ringoniella*), codling moth (*Cydia pomonella*), light brown apple moth (*Epiphyas postvittana*) and tufted apple bud moth (*Platynota idaeusalis* (Walker)). The apple leafminer, *Phyllonorycter (Lithocolletis) ringoniella* Matsumura (Lepidoptera: Gracilariidae), is an important insect pest on apple trees and has four to six generations a year in Korea, Japan, and China [3,4]. The infestation of this insect generally has shown on narrow host fruit trees to some of the pomes and stone fruits such as apple, cherry, peach, pear, and plum. Ever since 1990s, the outbreak of infestation caused by *P. ringoniella* has been widely observed in some outbreak years to be more

than 80% leaf damage into the major apple-growing regions in China [5]. The larvae of *P. ringoniella* mine on the underside of the leaf and also pupate inside it. The early infestations of this insect shows a greenish-white appearance on the upper surface and the irregular shape of silvery-green spots on the lower surface of the leaf [6]. Reduction in the photosynthetic area, inhibits the growth of new buds, defoliation of plants and premature ripening and fruit droppings are the damages caused by the mines done by the larvae of *P. ringoniella* [6,7]. To control the infestation of the apple leaf miner by chemical sprays of insecticides have a limited effect as the larva of *P. ringoniella* is an internal feeder of the leaf and has disadvantages owing to less nutrition. The organic growers all around the world demand non-chemical tactics to reduce the population of the apple leaf miner as well as the other lepidopteran insects. In Integrated Pest management, the use of semiochemical has a great potential in controlling, suppressing or eradicating the insect population by monitoring, mass trapping, mating disruption, lure and kill techniques [8]. In the insect sex pheromones, the (E,Z)-diene isomers are well-known, and responsible for special functions and the efficacy for the attraction of moths in the field [9,10]. The synthetic pheromone's efficiency is entirely based on its stereoisomeric purity [11].

The sex pheromone of the apple leaf miner *P. ringoniella* was identified by Ujiye *et al.* (1986) to be a blend of 10-tetradecenyl acetate and a non-conjugated tetradecadienyl acetate, with a double bond in position 10 [12]. The synthesis of the geometrical isomers of the pheromone was carried

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