REINVESTIGATION CONFIRMS ACTION OF Δ11-
DESATURASES IN SPRUCE BUDWORM MOTH SEX
PHEROMONE BIOSYNTHESIS

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Abstract—The biosynthesis of a large number of sex pheromone components of various moth species has been shown to start with common fatty acids and involve chain shortening by two carbons and introduction of a double bond at the 11–12 position. A recent report indicates that one of these common components, (E)-11-tetradecenyl acetate, is present in the eastern spruce budworm, Choristoneura fumiferana, but is not made by this pathway. Reinvestigation of this insect using in vivo and in vitro techniques indicates that the acetate indeed is made by a sequence of reactions similar to that used in other leafroller moths. In fact, evidence was found for the presence of several Δ11-desaturase systems in spruce budworm. One produced a large quantity of (Z)-11-hexadecanoic acid, and another produced (E)-11-tetradecanoic acid. It is not known if the small amount of (Z)-11-tetradecanoic acid is produced by either of those two systems or by a third system. A comparison with other species showed that cabbage looper moths have only the first system, red-banded leafroller moths use the last two systems, and European corn borer moths have all three.

Key Words—Spruce budworm, Choristoneura fumiferana, sex pheromone biosynthesis, Δ11-desaturase, Trichoplusia ni, Argyrotaenia velutinana, Ostrinia nubilalis, Lepidoptera, Tortricidae, Noctuidae, Pyralidae.

INTRODUCTION

The biosynthesis of many lepidopterous sex pheromone components has been shown to involve the reaction of common fatty acids with two key enzyme systems (Roelofs and Bjostad, 1984). These include microsomal β-oxidation to give limited chain shortening by two carbons, and a Δ11-desaturase to yield
acids with unsaturation at the 11-12 position. A variety of compounds is produced by varying (1) the length of the starting fatty acids (normally between 12 and 18 carbons), (2) the order in which the chain shortening and desaturation steps occur, (3) the number of times chain shortening occurs, (4) the stereochemistry of the unsaturated products, and (5) the functionality (alcohol, acetate, aldehyde) of the pheromone components, which are finally produced by reducing the acid precursors.

A good example of these key steps is given by the biosynthetic routes for the cabbage looper moth (CL), *Trichoplusia ni*, pheromone components. In this species the Δ11-desaturase system produces large quantities of Z11-16:Acid\(^1\) and Z11-18:Acid from palmitic and stearic acid, respectively. These are chain shortened to give pheromone precursor acids Z9-14:Acid and Z7-12:Acid from the former, and Z7-14:Acid and Z5-12:Acid from the latter (Bjostad and Roelofs, 1983). The Δ11-desaturase enzyme from CL was partially purified from the microsomal fraction and found to have a substrate specificity for 16- and 18-carbon acids (Wolf and Roelofs, 1986). However, in the redbanded leafroller moth (RBLR), *Argyrotaenia velutinana*, the Δ511-desaturase enzyme produces unsaturated 14-carbon acids from myristic acid in an E/Z ratio of ca. 3/2 (Bjostad and Roelofs, 1981). These are reduced to give a specific 8:92 ratio of the pheromone components, E11- and Z11-14:OAc.

Recently, Morse and Meighen (1984, 1986) indicated that the eastern spruce budworm (SBW), *Choristoneura fumiferana*, does not utilize the Δ11-desaturase enzyme system for production of the E11- and Z11-14:OAc found in their pheromone glands as precursors to the corresponding aldehyde pheromone components. Their data did not support a specific desaturation of myristic acid to give Δ11-14:Acid, and so they suggested that the pheromone was produced by some unspecified pathway, perhaps starting directly from acetate.

We found it surprising that there were two different biosynthetic pathways for E11- and Z11-14:OAc in two leafroller moth species. It was difficult to accept an alternate route in the case of SBW also because Dunkleblum et al. (1985) had shown that the SBW pheromone glands contain both 14- and 16-carbon Δ11-unsaturated fatty acyl moieties, indicating the presence of a Δ11-desaturase in their pheromone gland. Thus we decided to reinvestigate the biosynthesis of the E11- and Z11-14:OAc in SBW by both in vivo and in vitro techniques.

Since the SBW apparently desaturated both 14- and 16-carbon acids, we also conducted a comparative study with the Δ11-desaturase system of other species, such as the CL moth (specific to 16- and 18-carbon acids), the RBLR moth (specific to 14-carbon acids), and two strains of the European corn borer

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\(^1\) Specific compounds will be referred to by an abbreviated naming system, where a letter (Z or E) indicates the stereochemistry, the first number gives the site of unsaturation, the second number the chain length, and symbols indicate the oxygen function. Thus Z9-18:Acid is the abbreviation for oleic acid.