DEFENSIVE SECRETION OF CHRYSOMELID LARVAE
Linaeidea aenea LINNÉ and Plagiodera versicolora distincta Baly

FUMIO SUGAWARA, 2 KAZUHIRO MATSUDA, 3
AKIO KOBAYASHI, 2 and KYOHEI YAMASHITA 2

2Department of Agricultural Chemistry, Faculty of Agriculture
Tohoku University, Sendai, Japan
3Laboratory of Applied Entomology, Faculty of Agriculture
Tohoku University, Sendai, Japan

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Abstract—The larval defensive secretions of Linaeidea aenea Linné and
Plagiodera versicolora distincta Baly were identified as plagiolactone and
epiplagiolactone. In addition to these compounds, chrysomelidial and
the acetates of hexadecanol, octadecanol and (Z)-11-eicosenol from the former
insect, and plagiodial and epi-chrysomelidial from latter insect were
identified.

Key Words—Defensive secretion, Linaeidea aenea Linné, Plagiodera ver-
sicolora distincta Baly, chrysomelidial, plagiolactone, plagiodial.

INTRODUCTION

Recently chrysomelidial (I) and its epimer II, the novel cyclopentanoid mono-
terpenes, were identified in the defensive secretion of Plagiodera versicolora
(Meinwald et al., 1977) and Gastrophyrsa cyanea Melsheimer (Blum et al.,
1978). Plagiolactone (III) was also isolated from P. versicolora (Meinwald et
al., 1977). In previous studies (Sugawara et al., 1978; 1979), chrysomelidial (I)
and the acetates of octadecanol and (Z)-11-eicosenol were identified as defen-
sive substances from Gastrophyrsa atrocyanea Motschulsky and Phaedon
brassicae Baly.

1This is report No. 3 of the Defensive Secretion of Chrysomelid Beetles. Report No. 2 is
Sugawara et al., 1979.
In this paper, the defensive secretions of the larvae of two Japanese leaf beetles were investigated. *Linaeidea aenea* Linné, which feeds on alder leaves, secretes I, III, IV; and the acetates of hexadecanol, (Z)-9-octadecenol, octadecanol, and (Z)-11-eicosenol. Willow feeding *Plagiodera versicolora distincta* Baly also secretes cyclopentanoid monoterpenes II, III, IV, and a new isomer of I, named plagiodial (V) [5-(1-formylethyl)-2-methyl-2-cyclopentene-1-carbaldehyde] as a major component in the secretion. This report also describes the optimum conditions for the separation of these compounds (I or II, III, IV, and V) by gas chromatography.

**METHODS AND MATERIALS**

*L. aenea* were selected from our laboratory culture maintained on *Alnus hirsuta* Turcz leaves.

*P. versicolora distincta* were reared on *Salix bobylonica* L. leaves. The secretion from 350 *Linaeidea* larvae was collected by the previously described method (Sugawara et al., 1978) and weighed (45.4 mg). It was extracted with pentane, and dried over Na$_2$SO$_4$ to give 5.3 mg of the extracts. In the same way, 4.6 mg of extract was obtained from 50.2 mg of the secretions of 2700 *Plagiodera* larvae. *R*$_f$ values on TLC were calculated for 5-cm $\times$ 20-cm glass plate (silica gel) developed with hexane-ether (1:1). A Hitachi gas chromatograph 163 equipped with FID was employed with the following columns: column I—30-m $\times$ 0.25-mm glass capillary column (coated with OV-101) at 150°C with a flow rate of 2 ml/min; column II—2-m $\times$ 2.5-mm glass column (packed with 5% DEGS) at 200°C with a flow rate of 20 ml/min; column III—column I was used under programed temperature from 200 to 220°C at the rate of 1°C/min. Quantitative ratios were calculated from their peak areas relative to that of chrysomelidial (retention time = 9.3 min, column II) and are expressed in parentheses after each retention time. PMR spectra were recorded on a JEOL JNM PS-100 (100 MHz) spectrometer using CDCl$_3$ as