Lepidopterous Sex Attractants

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Up to date, many sex pheromones have been isolated from lepidopterous insects and characterized. Roelofs has successfully discovered new sex attractants for thirty seven lepidopterous species by field screening tests¹⁾ and, later, for more species by the combination of field tests and the EAG method.²⁾ Most of them belong to a group of normal primary alcohols or respective acetates with ten to sixteen carbons and one or two double bonds. Several thousand lepidopterous species are known to be distributed in Japan, some of them being native in Japan and different from those of foreign countries. However, only few informations on sex pheromones of these native insects have been known.

We planned to synthesize all the possible long chain ($C_{10} \sim C_{16}$) monoene*² alcohols and their acetates containing a double bond at higher positions than C-5 and to test their biological activity in fields. This paper deals with the preliminary results of the field test on twenty seven acetates.

All the chemicals were synthesized in our laboratory in the following way. The coupling reaction of an alkyl halide and a lithium acetylide in dioxane and the successive stereoselective hydrogenation of the acetylene group over Pd-BaCO₃ poisoned with pyridine yielded a *cis*-isomer, and the Birch reduction with lithium in ethylamine yielded a *trans*-isomer. One mg of each chemical to be tested was

applied to a rubber cap.*³ These caps were placed in Pherocon 1C traps,*³ which were set in three different field environments (see Table), from July to December of 1974. The caps were renewed at mid-July and early-September and the traps were checked on every ten days.

The results of the field tests are summarized in Table I. Males of nineteen lepidopterous species including four unidentified and two undescribed species were attracted by twelve chemicals. This result indicates that monoene acetates constitute one group of main sex pheromones of the Lepidoptera, supporting Roelofs' suggestion.²⁾

Among twelve active chemicals, each of seven chemicals showed activity to two different species. It is interesting to note that both *Telorta divergens* Butler (Noctuidae) and *Amphipyra monolitha* Guenée (Noctuidae) were attracted to *cis*-11-hexadecenyl acetate. However, the former was attracted from late-October to mid-November, while the latter from mid-September to mid-October. Furthermore, *Sathrobrotia* sp. (Cosmopterygidae) was attracted to *trans*-11-tetradecenyl acetate in Ibaragi Prefecture, while *Cosmopterygidae* sp. was attracted to the same chemical in Tokyo. It is suggested that different seasonal cycles and habitat preferences can result in the reproductive isolation among some lepidopterous species attracted by the same chemicals, if the attractants are real sex pheromones.

It must be pointed out that certain chemicals attracted some different species simultaneously. For example, *Cryptophlebia ombrodelta* Lower (Tortricidae) and *Pammene nemorosa* V. Kuznetsov (Tortricidae) were attracted to *cis*-8-dodecenyl acetate in Ibaragi Prefecture, and *Hoshinoa longicellanus* Walsingham (Tortricidae) and Tortricidae sp. to *cis*-11-tetradecenyl acetate in Tokyo. In the reproductive isolation of these species, other factors than attractants, namely, diurnal cycles and/or other chemicals and/or physical stimuli, may play important roles.

It is necessary to make clear the relationship

*² One diene acetate, *cis*-9, *trans*-12-tetradecenyl acetate, was also synthesized and tested.

*³ They were kindly supplied by Dr. J. Siddall of Zoecon Co.

TABLE I. NEW SEX ATTRACTANTS DISCOVERED IN FIELD SCREENING TESTS FROM JULY TO DECEMBER OF 1974

The field tests were done in the three different environments, (I) a rice field in Akita Prefecture (Ōmagari-shi), (II) a chestnut orchard in Ibaragi Prefecture (Ami-machi and Chiyoda-mura) and (III) a forest in Tokyo (Hachioji-shi). The chemical formulae are symbolized by *c=cis*, *t=trans*, the first number gives the position of unsaturation, the last number gives the carbon atoms in the chain and OAc=acetate.

FAMILY Species	Attractant	Place and Time of Flight						number of the attracted moths
		June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COSMOPTERYGIDAE <i>Cosmopterix</i> sp. <i>Sathrobrotia</i> sp. Gen. et sp.	c 9-12:OAc t11-14:OAc t11-14:OAc	I-III I I	I-III I I	II II II	II II II			198 882 329
GELECHIIDAE Gen. et sp. Gen. et sp.	c 5-12:OAc t 5-12:OAc			II II	II II	II, III II, III		820 16
TORTRICIDAE <i>Lobesia aeolopa</i> Meyrick ^{a)} <i>Cryptophlebia ombrodelta</i> Lower ^{a)} <i>Pamene nemorosa</i> V. Kuznetsov ^{a)} <i>Aphania auricristana</i> Walsingham ^{a)} Gen. et sp.	c 7-10:OAc c 8-12:OAc c 8-12:OAc c 9-14:OAc c11-14:OAc c11-14:OAc	III I I I I I	II II II II II II	II II II II II II	II II II II II II	II II II II II II		99 184 34 62 8 496
<i>Hoshinoa longicellanus</i> Walsingham ^{b)}	c11-14:OAc	II III III	I I I	II II II	II II II	II II II	II II II	110
PTEROPHORIDAE <i>Nippoptilia issikii</i> Yano	c 7-12:OAc			II II II	II II II	II II II	II II II	50
EPIPLEMIDAE <i>Epiplema moza</i> Butler	t11-16:OAc			III III III	III III III	III III III	III III III	9
NOCTUIDAE <i>Hermonassa cecilia</i> Butler ^{c)} <i>Telorta divergens</i> Butler ^{d)} <i>Telorta edentata</i> Leech ^{d)} <i>Orthogonia sera</i> Felder ^{e)}	c 9-14:OAc ^{f)} c11-16:OAc ^{g)} t11-16:OAc ^{g)} c 7-12:OAc				III III III	III III III	II II II	29 5 6
<i>Amphipyra monolitha</i> Guenée ^{e)} <i>Rusidrina depravata</i> Butler ^{e)}	c11-16:OAc c9, t12-14:OAc	I I			III III	III III	II II	6 56

a) Olethreutinae, b) Tortricinae, c) Noctuidae, d) Cuculinae, e) Amphipyridae, f) a few moths were attracted to c9, t12-14:OAc, g) a few moths were attracted to its geometrical isomer.

between new attractants and real sex pheromones. The biological activity of other synthetic chemicals will be reported in future.

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