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Posticlure: a novel *trans*-epoxide as a sex pheromone component of the tussock moth, *Orgyia postica* (Walker)

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Abstract—A single EAG-active component was found in a pheromone extract from virgin females of the tussock moth, *Orgyia postica*. This compound named posticlure possesses a *trans*-epoxy ring and was identified as (6*Z*,9*Z*,11*S*,12*S*)-11,12-epoxyhenicosa-6,9-diene by means of GC-MS, ^{1}H NMR and chiral HPLC analyses, and further chemical derivation followed by the GC-MS analysis. In a field test with the pheromone synthesized stereoselectively, the male moths were specifically attracted to the (11*S*,12*S*)-isomer but not to the antipode. © 2001 Elsevier Science Ltd. All rights reserved.

The tussock moth, *Orgyia postica* (Walker) (Lepidoptera: Lymantriidae), is one of the severe pests on mango and litchi in Okinawa, Japan.[1] Larvae are covered with bristles and can irritate human skin. They occasionally defoliate plants and cause considerable damage. The female moths are wingless, so they release a sex pheromone in order to attract males, copulate and lay eggs on the cocoon from which they emerged. The synthetic pheromone would be useful for mating disruption and population monitoring for control of this pest.

Larvae of *O. postica* were collected in mango fields in Okinawa and reared on an artificial diet[2] in the laboratory. A solvent extract of the sex pheromone glands was obtained from ca. 600 virgin females. The extract was analyzed with a capillary GC linked directly to electroantennographic (EAG) recording[3] from the

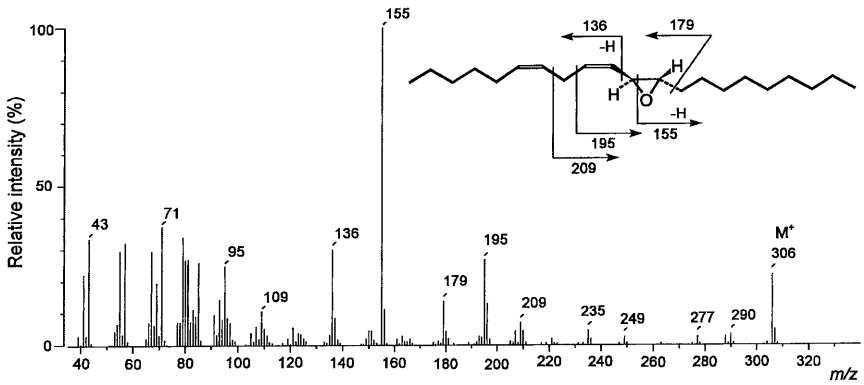

Figure 1. EI mass spectrum of natural posticlure (6*Z*,9*Z*)-*trans*-11,12-epoxyhenicosa-6,9-diene.

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antenna of a male *O. postica*. Single EAG response was observed at Kovat's Index (KI) 2548 on a polar HP-INNOWax column, and KI 2200 on a non-polar HP-1 column. The EAG-active compound was eluted gas-chromatographically as an almost pure material with 5% ether in *n*-hexane from column chromatography using 200 mg of Florisil. The EAG response coincided well with an FID peak on the GC, which was predominant in the fraction that represented approximately 17 ng per female abdominal tip.

On a GC-MS analysis operated in an EI mode, the EAG-active compound showed a mass spectrum (Fig. 1) similar to that of an unsaturated epoxide with a distinct molecular ion at m/z 306 (M^+, 21%, base m/z 155) and diagnostic ions at m/z 290 ($[M-16]^+$, 3.2%) and 288 ($[M-18]^+$, 2.6%). The Kovat's Indices (KI and ΔKI) supported this interpretation. Micro-scale reduction of ca. 85 ng of the compound with diimide[4] at 65°C for 1 h produced a single compound that gave a mass spectrum typical for a mono-epoxide with a C_{21} straight chain; m/z 310 (M^+, 7.3%, base m/z 83), 294 ($[M-16]^+$, 3.7%), 292 ($[M-18]^+$, 0.9%), 183 (65%), and 169 (62%). The latter two ions indicated the epoxy ring at the 10,11-position. The KI value (2467) on the polar HP-INNOWax column was almost the same to that for the *trans*-isomer (2468) of synthetic 10,11-epoxyhenicosane but different from that for the *cis*-isomer (2484).

The EAG-active compound (ca. 85 ng) was partially hydrogenated, in order to produce two mono-unsaturated epoxides, by reaction with diimide at 55°C for 1 h. Since preparation of their dimethyl disulfide (DMDS) derivatives[5] was unsuccessful, this derivation was accomplished after conversion of the epoxides to secondary alcohols by $LiAlH_4$ reduction. The products were subjected to GC-MS analysis. Mass spectra of one derivative showed a molecular ion at m/z 404 (22%) and a diagnostic ion at m/z 173 (base), which indicated the original double bond to be at 9-position, although the other diagnostic ion at m/z 231 was not observed probably because of the effect of the alcohol group. Another DMDS derivative showed diagnostic ions at m/z 273 (65%) and 131 (base), and indicated the double bond at 6-position.

The ^{1}H NMR spectrum of accumulated EAG-active component (ca. 8.5 μg from 500 females) (Fig. 2) showed the presence of two epoxide protons [δ 2.82 (1H, dt), 3.36 (1H, dd)], in which a coupling constant of $J=2.2$ Hz confirmed the *trans*-epoxide structure. Four vinyl proton signals [δ 5.07 (1H, ddd), 5.36 (1H, dtt), 5.44 (1H, dtt), 5.66 (1H, dt)] and one doubly allylic proton signal [δ 2.96 (2H, dd)] were also observed. The COSY spectrum confirmed the partial structure shown in Fig. 2, and it guided us to only one possible structure, (6*Z*,9*Z*)-*trans*-11,12-epoxyhenicosa-6,9-diene. We would like to propose to name this novel pheromone 'posticlure', in reference to the species name.

Posticlure has stereoisomerism, that is, 11*S*,12*S* and 11*R*,12*R* configurations are possible. Both enantiomers were stereoselectively synthesized using a Sharpless epoxidation[6] of *trans*-allylic alcohol derived from *n*-decanal as a key reaction. The chiral epoxidation employing (+)-diethyl tartrate produced an optically active epoxy intermediate, which was converted to (11*S*,12*S*)-posticlure with 59% e.e. (Fig. 3). The antipode was prepared by employing (−)-diethyl tartrate. Preparative HPLC with a chiral column (Chiralpak AD) furnished optically pure samples, which showed almost the same ^{1}H NMR, GC-MS and GC data as those of the EAG-active compound.

On this chiral HPLC, the natural pheromone showed only one peak with the same retention time of synthetic (11*S*,12*S*)-posticlure. Furthermore, males were captured by this (11*S*,12*S*)-isomer but not by (11*R*,12*R*)-isomer in field experiments conducted in Okinawa in June 2000. These results led to the assignment of the 11*S*,12*S* configuration to the natural sex pheromone of *O. postica* females.

Many mono-epoxy compounds derived from (3*Z*,6*Z*,9*Z*)-trienes and (6*Z*,9*Z*)-dienes, which are biosynthesized from linolenic and linoleic acids, have been identified as sex pheromone components secreted by females in several families of Lepidoptera.[7,8] Males of many more species were found to be attracted to the synthetic epoxides.[9] All those epoxides, however, have a *cis*

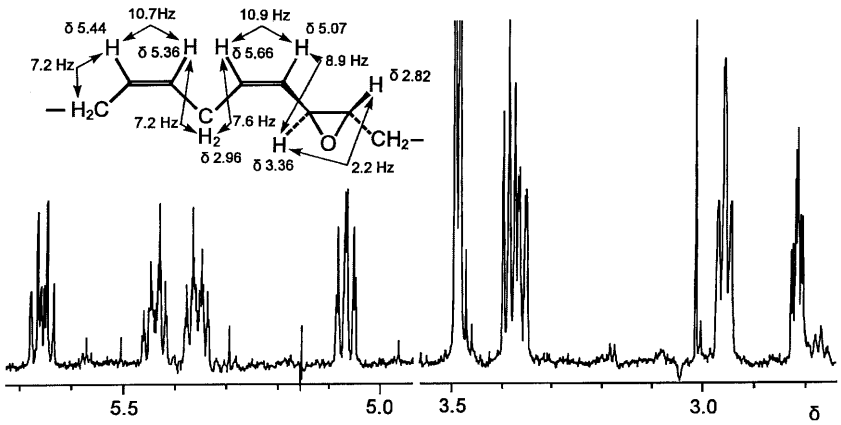

Figure 2. ^{1}H NMR spectrum of natural posticlure (6*Z*,9*Z*)-*trans*-11,12-epoxyhenicosa-6,9-diene. Signals at δ 3.38 and δ 3.49 are unrelated. These were not observed for synthetic posticlure.

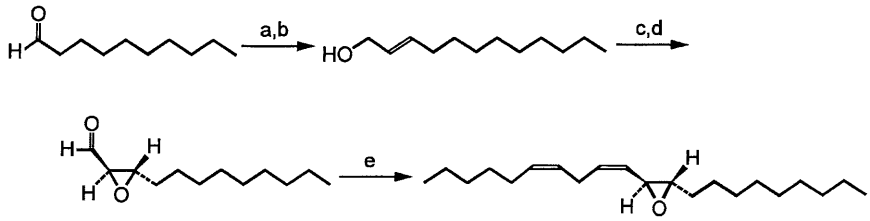

Figure 3. Synthetic route of (11*S*,12*S*)-posticlure. Reagents: (a) $Ph_3P{=}CHCO_2Me$; (b) $LiAlH_2(OEt)_2$; (c) $Ti(O\textit{i}\text{-}Pr)_4$, (+)-DET, $\textit{t}\text{-}BuO_2H$; (d) PCC; (e) $(Z)\text{-}Ph_3P{=}CHCH_2CH{=}CH(CH_2)_4CH_3$.

configuration. To our knowledge, this is therefore the first pheromone with a *trans*-epoxy ring so far as we know. It should provide us with an interesting focus for biosynthetic study, and also a useful tool for plant protection.

Acknowledgements

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