Journal of Chemical Ecology, Vol. 13, No. 6, 1987

CHIRALITY OF MACROLIDE PHEROMONES OF GRAIN BEETLES IN THE GENERA *Oryzaephilus* AND *Cryptolestes* AND ITS IMPLICATIONS FOR SPECIES SPECIFICITY[1]

A.C. OEHLSCHLAGER,[2] G.G.S. KING,[2] H.D. PIERCE, JR.,[2] A.M. PIERCE,[2] K.N. SLESSOR,[2] J.G. MILLAR,[2] and J.H. BORDEN[3]

[2]*Department of Chemistry*
[3]*Centre for Pest Management, Department of Biological Sciences*
Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

(Received April 28, 1986; accepted September 22, 1986)

Abstract—The chiralities of macrolide lactone aggregation pheromones of five species of economically important grain beetles have been determined by capillary gas chromatographic separation of the diastereomeric (*S*)-*O*-acetyllactate derivatives of the hydroxy methyl esters derived from boron trifluoride-catalyzed cleavage of the macrolides in methanol. Chirally pure (*Z*)-3-dodecen-11-olide (I) is produced in the *S* configuration by *Cryptolestes ferrugineus* (Stephens) and in the *R* configuration by *Oryzaephilus mercator* (Fauvel). (*Z,Z*)-3,6-Dodecadien-11-olide (II) is produced in the *R* configuration by both *O. mercator* and *O. surinamensis* (L.). (*Z,Z*)-5,8-Tetradecadien-13-olide (IV) is produced in the *R* configuration by *O. surinamensis* and as a 85 : 15 mixture of *R* and *S* isomers by *C. turcicus*. (*Z*)-5-Tetradecen-13-olide (V) is produced in the *S* configuration by *C. pusillus* (Schönherr) and as a 33 : 67 mixture of the *R* and *S* isomers by *C. turcicus* (Grouvelle). The results indicate that in these cucujids, species specificity in pheromone response is maintained at least in part by pheromone chirality.

Key Words—Chiral semiochemicals, pheromones, enantiomeric composition, enantiomeric synergism, *Cryptolestes ferrugineus, Cryptolestes pusillus, Cryptolestes turcicus, Oryzaephilus mercator, Oryzaephilus surinamensis,* Coleoptera, Cucujidae, (*Z*)-3-dodecen-11-olide, (*Z,Z*)-3,6-dodecadien-11-olide, (*Z*)-5-tetradecen-13-olide, (*Z,Z*)-5,8-tetradecadien-13-olide.

[1] Research supported by the Natural Sciences and Engineering Reseach Council of Canada, Operating Grants A3881, A0851 and A3785, and Strategic Grant G0958.

0098-0331/87/0600-1543$05.00/0 © 1987 Plenum Publishing Corporation

INTRODUCTION

Since the first discovery of an aggregation pheromone response in cucujid grain beetles (Borden et al., 1979), our investigations in the genera *Cryptolestes* and *Oryzaephilus* have yielded a new class of aggregation pheromones, the macrolide lactones. In the five economically important species studied, we found seven macrolide pheromones (Table 1) (H.D. Pierce, Jr. et al., 1984). Laboratory bioassays revealed that for each species, insects of mixed sex are attracted best to those mixtures of macrolides produced by feeding males (H.D. Pierce, Jr. et al., 1984). In four species, superior attraction was achieved with binary mixtures (Wong et al., 1983; Millar et al., 1985a, b; A.M. Pierce, et al., 1984; Pierce et al., 1985), whereas for *Oryzaephilus surinamensis* (L.), a ternary mixture of macrolides was maximally attractive (A.M. Pierce et al., 1984; Pierce et al., 1985). The males of some species produce macrolides that are pheromones for other species (Table 1). In some instances, different species share common pheromones. Maintenance of species recognition in this sympatric group must therefore involve several mechanisms.

We report the determination of the chiralities of the male-produced macrolides in five species of cucujids. This information, in combination with previously reported bioassay data, allows delineation of the role of chirality in maintenance of species recognition.

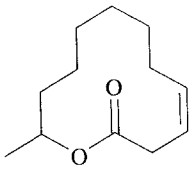
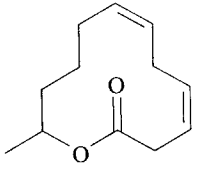
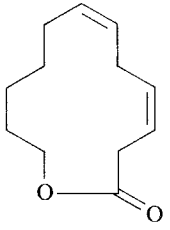
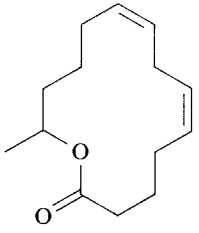
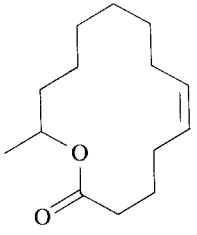
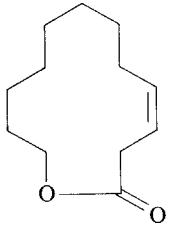
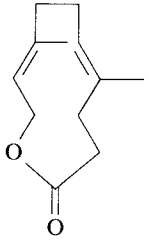
METHODS AND MATERIALS

Synthetic Macrolides. Synthetic I in both its racemic and chiral forms was available from previous studies (Oehlschlager et al., 1983). Synthetic racemic II and IV and synthetic chiral IV were prepared as described by Millar and Oehlschlager (1984). Racemic and chiral V were prepared as described by Millar et al. (1983). The remaining macrolides (III, VI and VIII) in Table 1 are achiral and were previously prepared in the references mentioned above.

Insect-Derived Macrolides. Pentane extracts of Porapak Q collected volatiles from feeding adults of each species were prepared as previously described (H.D. Pierce, Jr. et al., 1984). The macrolide composition as determined by gas chromatography (GC) of each extract is given in Table 1.

Derivation of Macrolides and Analysis. Synthetic macrolides or Porapak Q extracts of beetle-produced volatiles (0.5–5.0 μg) were dissolved in methanol (50–100 μl) containing 5% boron trifluoride etherate at $-20°C$ and sealed in glass ampoules. The reactions were maintained at 70°C overnight. This process yielded the corresponding hydroxyl methyl esters, which were isolated by dilution of each reaction with pentane (100 μl) and washing with water (3 $\times$ 50 μl). The pentane solution was dried over finely powdered sodium sulfate and filtered through glass wool. A portion (30 μl) of the filtrate was derivatized by treatment in a clean ampoule with pyridine (15 μl of a 50 mg/ml solution in

TABLE 1. DISTRIBUTION OF MACROLIDES IN *Cryptolestes* AND *Oryzaephilus* SPECIES[a]

	Distribution (%)						
	 I	 II	 III	 IV	 V	 VI	 VII
C. ferrugineus	34 P	2	—	0.5	3.5	—	60 P
C. pusillus	—	—	1.5	—	2.5 P_{syn}	96 P	—
C. turcicus	—	—	—	72 P	28 P_{syn}	—	—
O. mercator	45 P	55 P	1	<0.1	<0.1	—	—
O. surinamensis	—	16 P	33 P	51 P_{syn}	<0.1	—	—

[a]Composition of macrolide fraction determined by gas chromatographic analysis of captured volatiles from insects of mixed sex (only males of each species produce pheromones) feeding on rolled oats (A.M. Pierce, et al., 1984; H.D. Pierce, Jr. et al., 1984). P = pheromone; P_{syn} = pheromones inactive alone but which act as synergists. Pheromones active in bioassays conducted on insects of mixed age and sex. − = Not detected in species by single ion monitoring of the most prominent fragment ion in the mass spectrum of the macrolide when the macrolide fraction was subjected to GC-MS. Probable detection limits 0.01%. Chemical names of I–VII are as follows: I: (*Z*)-3-dodecen-11-olide; II: (*Z*, *Z*)-3,6-dodecadien-11-olide; III: (*Z*, *Z*)-3,6-dodecadienolide; IV: (*Z*, *Z*)-5,8-tetradecadien-13-olide; V: (*Z*)-5-tetradecadien-13-olide; VI: (*Z*)-3-dodecenolide; VII: 4,8-dimethyl-(*E*,*E*)-4,8-decadien-10-olide.

TABLE 2. RETENTION TIMES OF MACROLIDES, DERIVED HYDROXY METHYL ESTERS, AND THEIR (*S*)-*O*-ACETYLLACTATE DIASTEREOMERS[a]

Macrolide	Source	Column and temp. program[b]		Retention time (min)[b]			
						(*S*)-*O*-Acetyllactates	
		DB-1	SPB5	Macrolide	Hydroxy methyl ester	*R* macrolide	*S* macrolide
1 (*R*, *S*)-I	Synthetic	1		15.16	19.50	29.99	30.42
2 (*S*)-I	Synthetic	1		15.16	19.52	30.05 (<1%)	30.49 (>99%)
3 (*S*)-I	*C. ferrugineus*	1		15.20	19.48	ND[c]	30.45
4 (*R*, *S*)-I	Synthetic		1	9.81	13.63	21.93	22.31
5 (*R*)-I	*O. mercator*		1			21.86	ND
6 (*R*, *S*)-II	Synthetic		1	9.81	13.42	21.47	21.80
7 (*R*)-II	*O. mercator*		1			21.38	ND
8 (*R*)-Dihydro-I	*O. mercator*		1			22.13	ND
9 (*R*)-Tetrahydro-II	*O. mercator*		1			22.12	ND
10 (*S*)-Dihydro-I	Synthetic		1			22.15(1%)	22.56(99%)
11(*R*,*S*)-Tetrahydro-II	Synthetic		1			22.15	22.55

12 (*R*)-Tetrahydro-II	*O. surinamensis*		1			22.14(99%)	22.51(1%)
13 (*R*, *S*)-IV	Synthetic		1	12.63	16.15	27.91	28.42
14 (*R*)-IV	Synthetic		1	12.62	16.24	27.89(96%)	28.36(4%)
15 (*R*,*S*)-IV	*C. turcicus*		1	12.61	16.18	27.85(85%)[d]	28.35(15%)[d]
16(*R*,*S*)-Tetrahydro-IV	Synthetic		1			30.12	30.80
17 (*R*)-Tetrahydro-IV	*O. surinamensis*		1			30.08	ND
18 (*R*)-Tetrahydro-IV	*O. surinamensis*	2				30.07	ND
19 (*R*,*S*)-V	Synthetic		1	12.63	16.31	28.75	29.30
20 (*R*)-V	Synthetic		1		16.47	28.68(94%)	29.26(6%)
21(*R*,*S*)-V	*C. turcicus*		1	12.61	16.35	28.69(34%)[d]	29.30(66%)[d]
22 (*R*,*S*)-V	Synthetic	2				28.92	29.35
23 (*R*)-V	Synthetic	2				28.92 (96%)	29.39 (4%)
24 (*S*)-V	*C. pusillus*	2				ND	29.35
25 (*R*,*S*)-Dihydro-V	Synthetic	2				29.97	30.41
26 (*S*)-Dihydro-V	*C. pusillus*	2				ND	30.40

[a] Analysis by coupled gas chromatography–mass spectrometry as previously described (Slessor et al., 1985) confirmed the identity of the observed peaks as the desired *O*-acetyllactate diastereomers (major fragment ions at *m/z* 115, 87, 43).

[b] Gas chromatographic conditions: Column DB-1: 30 m × 0.25 mm ID fused silica column programmed as follows: (1) 60°C for 2 min, 7°C/min to 180°C, 2°C/min to 240°C; (2) 80°C for 2 min, 10°C/min to 180°C, 2°C/min to 220°C. Column SPB5: 30 m × 0.25 mm ID fused silica column programmed as follows: (1) 100°C for 2 min, 10°C/min to 180°C, isothermal for 2 min, 10°C/min to 215°C.

[c] ND = not detected

[d] Average of three determinations.

ether) and (*S*)-*O*-acetyllactyl chloride (30 μl of a 25 mg/ml solution in methylene chloride), as described by Slessor et al. (1985).

The *O*-acetyllactyl methyl esters derived from synthetic and naturally occurring macrolides I, II, IV, and V were analyzed by capillary gas chromatography on Hewlett-Packard 5890 and 5880A instruments fitted with flame-ionization detectors. The injector and detector temperatures were 250°C. Helium was the carrier gas. Columns and oven temperature programs are listed in Table 2.

Microhydrogenations were performed by placing 30–50 μl of the hexane solution of the macrolides under one atmosphere of hydrogen in the presence of a few milligrams of 5% Pd on $BaSO_4$. The solution was separated from catalyst by syringe prior to treatment with $BF_3 \cdot CH_3OH$.

The chirality of I in *C. ferrugineus* (Stephens) was determined by comparison of the retention times (Table 2) for the *O*-acetyllactate derivatives (IX) derived from synthetic (*R*,*S*)-I (entry 1) and synthetic (*S*)-I (entry 2) with the *O*-acetyllactate derived from natural I produced by *C. ferrugineus* (entry 3). The same procedure was used for the determination of the chirality of IV in *C. turcicus* (Grouvelle) (entries 13–15), and of V in *C. turcicus* (entries 19–21) and *C. pusillus* (Schönherr) (entries 22–24).

Both I and II reduce to the same saturated macrolide. The determination of the chirality of I in *O. mercator* (Fauvel) involved reduction of natural I, isolated by micropreparative GC, to its dihydro derivative followed by the usual derivatization. Comparison of the retention times of the *O*-acetyllactate derivatives of synthetic racemic tetrahydro II (entry 11), synthetic dihydro (*S*)-I (entry 10) and dihydro (entry 8) derived from *O. mercator* yielded the configuration of the natural material. The retention values obtained above (Table 2) for the *O*-acetyllactate derivative of tetrahydro II (entry 11) enabled us to determine the chirality of tetrahydro II derived from reduction of II produced by *O. mercator* (entry 9) and *O. surinamensis* (entry 12). Likewise, both IV and V reduce to the same saturated macrolide. Knowledge of the chirality of V in *C. pusillus* (entry 24) from the experiments described above allowed assignment of the chirality of the corresponding *O*-acetyllactate of the dihydro derivative (entries 25, 26). This in turn can be used to assign chirality in the *O*-acetyllactate of tetrahydro IV derived from *O. surinamensis* (entry 18).

RESULTS AND DISCUSSION

Chirality of Macrolides I, II, IV, and V. Conversion of macrolides I, II, IV, and V to the corresponding hydroxyl methyl esters (VIII) and thence to *O*-acetyllactate derivatives (IX) is not accompanied by any apparent racemization of the chiral center or double bond isomerization as evidenced by the conversion of synthetic chiral macrolides to single diastereomers (Figure 1). Diastereomers

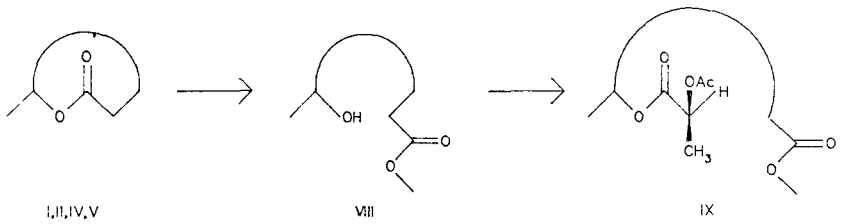


FIG. 1. Conversion of macrolide pheromones to *O*-acetyllactate methyl esters.

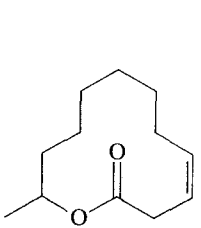
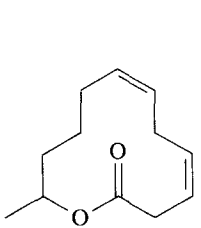
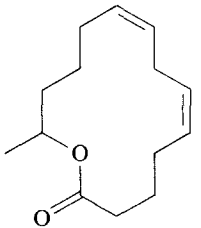
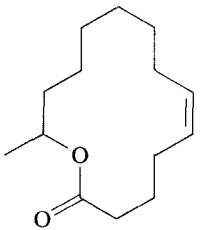
(IX) obtained from each racemic macrolide were baseline-separated by the chromatographic systems used. In all cases, the diastereomers (IX) derived from macrolides possessing the *R* configuration eluted prior to those derived from the corresponding macrolides possessing the *S* configuration. From previous work on this method, it is known that errors due to kinetic resolution during formation of the *O*-acetyllactates (IX) and to differential weight response of the diastereomers are less than 3% (Slessor et al., 1985). The enantiomeric compositions calculated for each macrolide in Table 3 are therefore not corrected for either of these variables.

Cross-Attractancy in Cucujids. The aggregation pheromone of the rusty grain beetle, *C. ferrugineus*, consists of I and VII (Wong et al., 1983). These two macrolides, each attractive alone, also act synergistically. One would not expect the rusty grain beetle to be cross-attracted (Table 4) to other cucujids in Table 1 for two reasons. First, *C. ferrugineus* is the only species that produces VII. Second, although both *C. ferrugineus* and *O. mercator* share I as a pheromone, the former produces (Table 3) and responds (Wong et al., 1983) only to (*S*)-I, whereas the latter produces (Table 3) and responds (Pierce et al., 1987) only to (*R*)-I.

The macrolide pheromones produced by *C. pusillus* are V and VI (Table 1) (Millar et al., 1985a). Macrolide V acts to synergize response to the second component, VI, which is active alone. Although *C. pusillus* produces (*S*)-V of high chiral purity (Table 3), no preference for one enantiomer of V acting as a synergist for VI was detected by laboratory bioassays (Millar et al., 1985a). Cross-attraction (Table 4) of *C. pusillus* to other cucujids in Table 1 is not expected since VI, a singly active pheromone component for this species, is not produced by any other species. Although V is common to all cucujids investigated, it is not attractive alone to *C. pusillus*.

The flour mill beetle, *C. turcicus*, utilizes IV and V as its aggregation pheromone (Table 1). As with *C. pusillus*, V is inactive alone but synergizes response to IV which is attractive alone (Millar et al., 1985b). Both IV and V are produced by *C. turcicus* as mixtures of *R* and *S* enantiomers and with opposite chiral enrichments. Macrolide IV is rich in *R* enantiomer (85:15, *R*:*S*)

TABLE 3. CHIRALITIES OF MACROLIDES OF *Cryptolestes* AND *Oryzaephilus* SPECIES[a]

	 I	 II	 IV	 V
C. ferrugineus	*S*			
C. pusillus				*S*
C. turcicus			*R*:*S*(85:15)	*R*:*S*(33:67)
O. mercator	*R*	*R*		
O. surinamensis		*R*	*R*	

[a]Single *S* or *R* indicates >99% one enantiomer.

and V is rich in *S* enantiomer (33:67, *R*:*S*). Careful analysis of the responses of *C turcicus* to the chiral isomers of the singly active macrolide, IV (Millar et al., 1985b), reveals that mixtures of IV containing both *R* and *S* isomers are more attractive than either chiral isomer alone. This is the only known case of enantiomeric synergism in the cucujids. Synergism between enantiomers also occurs in the scolytids, *Gnathotricus sulcatus* (Borden et al., 1976) and *Ips pini* (Lanier et al., 1980).

It is probable that *C. turcicus* would not be cross-attracted to *C. ferrugineus*, even though both IV and V are produced by the latter. In *C. turcicus*, the V:IV ratio is 0.38, whereas, in *C. ferrugineus*, it is 13.0. Furthermore, IV and V are only minor components of *C. ferrugineus* volatiles. Attraction of *C. turcicus* to *C. pusillus* would not be expected since both share only V which is inactive alone in both species. Attraction of *C. turcicus* to *O. mercator* is unlikely because both IV and V are produced by the latter only as minor components (Table 1). Attraction of *C. turcicus* to *O. surinamensis* would not be expected for two reasons. The ratio of IV to V produced by *O. surinamensis* (>510) is drastically different from that emitted by *C. turcicus*. Secondly, IV produced by and attractive to *C. turcicus* is a mixture of *R* and *S* enantiomers, whereas *O. surinamensis* produces (*R*)-IV of high chiral purity (Table 3).

The merchant grain beetle, *O. mercator*, utilizes macrolides I and II as its aggregation pheromone (Table 1; A.M. Pierce, et al., 1984; Pierce et al., 1985). Both I and II are active alone and additively (A.M. Pierce et al., 1984; Pierce et al., 1985). *O. mercator* produces (*R*)-I and (*R*)-II in high chiral purity (Table 3), and this species responds only to the *R* enantiomer of each component of its aggregation pheromone (Pierce et al., 1987). This species would not be expected to be attracted (Table 4) to *C. ferrugineus* because the latter produces only *S*-I (Table 3) (Wong et al., 1983). Cross-attraction of *O. mercator* to *O. surinamensis* is possible since both species produce (*R*)-II (Table 3) which is attractive alone to *O. mercator* (Pierce et al., 1987).

The sawtoothed grain beetle *O. surinamensis* utilizes only three macrolides (II, III, and IV) as pheromones (A.M. Pierce, et al., 1984; Pierce et al., 1985). Macrolides II and III are attractive alone and additively in 1:1 mixture, whereas IV is not attractive but synergizes response to II and III (H.D. Pierce, Jr. et al., 1984; Pierce et al., 1985).

O. surinamensis produces (Table 3) and responds (Pierce et al., 1987) to the *R* isomers of II and IV. Cross-attraction (Table 4) of *O. surinamensis* to *C. ferrugineus* due to the production of minor amounts of II and IV by the latter is not likely since the II:IV ratio in *C. ferrugineus* does not approximate that found in *O. surinamensis* (Table 1). Cross-attraction of *O. surinamensis* to *C. pusillus* is not likely since the only *O. surinamensis* pheromone produced by *C. pusillus* is III and this is a minor component in the volatiles of the latter. Attraction of *O. surinamensis* to *C. turcicus* would not be expected to occur

TABLE 4. CROSS ATTRACTION OF *Cryptolestes* AND *Oryzaephilus* SPECIES[a]

Responding species	Emitting species				
	C. ferrugineus	*C. pusillus*	*C. turcicus*	*O. mercator*	*O. surinamensis*
C. ferrugineus	+	– [1]Emits no VII	– [1]Emits no VII	– [1]Emits no VII [3]Emits *R*-I	– [1]Emits no VII
C. pusillus	– [1]Emits no VI	+	– [1,2]Emits no VI	– [1,2]Emits no VI	– [1,2]Emits no VI
C. turcicus	– [2]Emits insufficient IV relative to V Insufficient amounts of IV and V	– [1,2]Emits no IV	+	– Emits insufficient IV and V	– [2,4]Emits only *R*-IV
O. mercator	– [3]Emits only *S*-I	– [1]Emits no I or II	– [1]Emits no I or II	+	+ (moderate-good) Emits no I
O. surinamensis	– [1]Emits insufficient II	– [1]Emits no II or IV Insufficient III	– [2]Emits no II or III	+ (low) Emits insufficient IV, III relative to II	+

[a] 1 to 4 refer to corresponding mechanisms of species recognition as given in Conclusion. Macrolides listed refer to pheromone components identified as being required for response by responding species that are missing in emitting species. + = responding species is expected to be attracted to emitting species; – = responding species not expected to be attracted to emitting species.

even though these two species produce major amounts of IV. This component of the *O. surinamensis* pheromone blend is not attractive unless II and III are present (H.D. Pierce, Jr. et al., 1984; Pierce et al., 1985). Both of the latter components are absent in *C. turcicus* volatiles. Attraction of *O. mercator* to *O. surinamensis* is likely since each species uses (*R*)-II as an active pheromone component. In addition, *O. mercator* produces a minor amount of III which is singly a pheromone of low activity for *O. surinamensis*.

CONCLUSION

The only cucujid investigated to date likely to exhibit significant cross-attraction is *O. mercator* to *O. surinamensis* (Table 4). The group of insects investigated utilize several mechanisms for species recognition. The major mechanisms identified are: (1) presence of a unique pheromone (*C. ferrugineus*, VII; *C. pusillus*, VI); (2) use of synergistic pheromones that are inactive alone but synergize response to other pheromones (*O. surinamensis*, IV; *C. pusillus* and *C. turcicus*, V); (3) response to only one chiral isomer of a pheromone (*C. ferrugineus* and *O. mercator*, I); and (4) synergism between enantiomers of a pheromone (*C. turcicus*, IV).

REFERENCES

BORDEN, J.H., CHONG, L., MCLEAN, J.A., SLESSOR, K.N., and MORI, K. 1976. *Gnathotricus sulcatus*: Synergistic response to enantiomers of the aggregation pheromone sulcatol. *Science* 192:894–896.

BORDEN, J.H., DOLINSKI, M.G., CHONG, L., VERIGIN, V., PIERCE, H.D., JR., and OEHLSCHLAGER, A.C. 1979. Population aggregation pheromone in the rusty grain beetle, *Cryptolestes ferrugineus* (Coleoptera: Cucujidae. *Can. Entomol.* 111:681–688.

LANIER, G.N., CLAESSON, A., STEWART, T., PISTON, J.J., and SILVERSTEIN, R.M. 1980. *Ips pini*: The basis for interpopulational differences in pheromone biology. *J. Chem. Ecol.* 6:677–687.

MILLAR, J.G., and OEHLSCHLAGER, A.C. 1984. Synthesis of *Z,Z*-skipped diene macrolide aggregation pheromones for *Cryptolestes* and *Oryzaephilus* species. *J. Org. Chem.* 49:2332–2338.

MILLAR, J.G., OEHLSCHLAGER, A.C., and WONG, J.W. 1983. Synthesis of two macrolide pheromones from the flat grain beetle, *Cryptolestes pusillus*. *J. Org. Chem.* 48:4404–4407.

MILLAR, J.G., PIERCE, H.D., Jr., PIERCE, A.M., OEHLSCHLAGER, A.C., BORDEN, J.H., and BARAK, A. 1985a. Aggregation pheromones of the flat grain beetle, *Cryptolestes pusillus* (Coleoptera: Cucujidae). *J. Chem. Ecol.* 11:1053–1070.

MILLAR, J.G., PIERCE, H.D., JR., PIERCE, A.M., OEHLSCHLAGER, A.C., and BORDEN, J.H. 1985b. Aggregation pheromones of the grain beetle, *Cryptolestes turcicus* (Coleoptera: Cucujidae). *J. Chem. Ecol.* 11:1071–1081.

OEHLSCHLAGER, A.C., WONG, J.W., VERIGIN, V.G., and PIERCE, H.D., JR. 1983. Synthesis of two macrolide pheromones of the rusty grain beetle, *Cryptolestes ferrugineus*. *J. Org. Chem.* 48:5009–5017.

PIERCE, A.M., PIERCE, H.D., JR., MILLAR, J.G., BORDEN, J.H., and OEHLSCHLAGER, A.C. 1984. Aggregation pheromones in the genus *Oryzaephilus* (Coleoptera: Cucujidae), pp. 107–120, *in*

Proceedings of the Third International Working Conference on Stored-Product Entomology. Manhattan, Kansas.

PIERCE, A.M., PIERCE, H.D., JR., OEHLSCHLAGER, A.C., and BORDEN, J.H. 1985. Macrolide aggregation pheromones in *Oryzaephilus surinamensis* and *O. mercator* (Coleoptera: Cucujidae). *J. Agric. Food Chem.* 33:848–852.

PIERCE, A.M., PIERCE, H.D., JR., OEHLSCHLAGER, A.C.,, and BORDEN, J.H. 1987. Response of *Oryzaephilus surinamensis* and *O. mercator* to the chiral isomers of their macrolide aggregation pheromones. *J. Chem. Ecol.* 13:1525–1542.

PIERCE, H.D., JR., PIERCE, A.M., MILLAR, J.G., WONG, J.W., VERIGIN, V., OEHLSCHLAGER, A.C., and BORDEN, J.H. 1984. Methodology for isolation and analysis of aggregation pheromones in the genera *Cryptolestes* and *Oryzaephilus*, pp. 121–137, *in* Proceedings of the Third International Working Conference on Stored-Product Entomology. Manhattan, Kansas.

SLESSOR, K.N., KING, G.G.S., MILLER, D.R., WINSTON, M.L., and CUTFORTH, T.L. 1985. Determination of chirality of alcohol or latent alcohol semiochemicals in individual insects. *J. Chem. Ecol.* 11:1659–1667.

WONG, J.W., VERIGIN, V., OEHLSCHLAGER, A.C., BORDEN, J.H., PIERCE, H.D., JR., PIERCE, A.M., and CHONG, L. 1983. Isolation and identification of two macrolide pheromones from the frass of *Cryptolestes ferrugineus*. *J. Chem. Ecol.* 9:451–474.